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SOME CONSIDERATIONS IN DETERMINING THE ORIGIN OF ORE DEPOSITS OF THE MISSISSIPPI VALLEY TYPE[1]

ERNEST L. OHLE

ABSTRACT

New information since the publication of Special Paper 24 of the Geological Society of America in 1939 are reviewed. Consideration of the identifying characteristics of deposits of this type strongly suggests that all of them had the same general mode of origin and that consideration of the group as a whole rather than individually offers a better chance of determining what was that mode of origin.

IN 1939 the Geological Society of America published a summary of the geology of the ore deposits of the Mississippi Valley region. This volume (1), edited by E. S. Bastin, contained contributions from the foremost students of the area that described the regional geologic setting of the various deposits as well as the detailed geology as then known. The various ideas as to the origin of the ores were discussed with the general, though not unanimous, conclusion that the deposits were hydrothermal products. Only those deposits in the immediate Mississippi Valley area were considered without any attempt to introduce evidence from other districts generally accepted as being of the "Mississippi Valley type".

Since 1939, much new information has come from extended studies of two of the important districts described in the 1939 report and important extensions of the known ore have been found. Likewise, concentrated geologic efforts have been fruitful in several "Mississippi Valley type" districts—both in the United States and foreign—not treated in the 1939 paper. The wealth of new field information on the structural and stratigraphic relations of this interesting ore type, coupled with the results of theoretical and laboratory studies of the past 18 years, makes desirable a review of our present knowl-

[1] This paper was presented at the Annual Meeting of the A.I.M.E. and the Society of Economic Geologists in New York, February, 1958.

edge and interpretation of these important deposits, which for many years have yielded over 20 percent of the world's annual production of lead and zinc, together with large amounts of fluorspar and barite. No restatement of the details of the geologic evidence will be attempted here; the interested student is referred to the papers cited.

Figure 1 shows the distribution around the world of the deposits under consideration.

A principal thesis of these remarks is that there is so much similarity in all these deposits that it seems necessary for all of them to have had a similar mode of origin, whatever that may be. Variations in the shape, size and

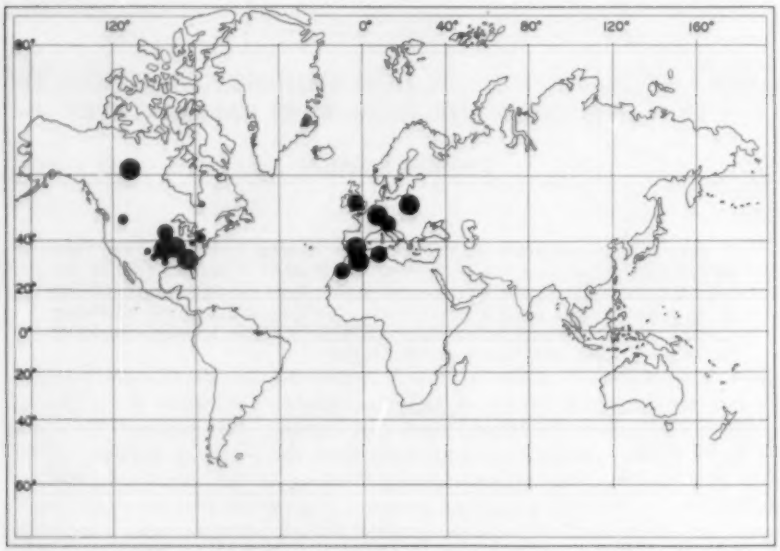

FIG. 1. World wide distribution of ore deposits of the Mississippi Valley type. The size of the circles indicates the relative productivity of the different areas.

mineralogy of the ore bodies give each district some individuality, but there are enough of the "typical" characteristics present in all cases to make classification in the "Mississippi Valley type" agreeable to most geologists. Thus, the overall process giving rise to the ore solutions surely was the same for all in the group. Either they all have igneous affiliations or they all do not.

Acknowledgment of this kinship between deposits in the various districts offers many advantages in trying to arrive at a decision as to just what the origin may have been, for the amount of guiding and limiting evidence that must fit into the hypothesis is greatly increased over that available in any one district. To a certain extent this was recognized by the authors of Special Paper 24 (1) in treating all of the immediate Mississippi Valley areas to-

gether; by expanding the consideration to include ore deposits of this type all over the world the chances of success, i.e., arriving at the correct answer, are improved several fold. Since most of these districts are quite simple structurally, a number of hypotheses might fit the facts in any one of them, but if the facts to be met can safely be drawn from all the districts, then the explanations that will fit all of the data are much less numerous. One purpose of this paper is to call attention to the field facts that have been reported from the various areas that seem to have an important bearing on the kind of ore fluid that was responsible for the ore and on the way it circulated.

SUMMARY OF INVESTIGATIONS AND PUBLICATIONS, 1939–1957

Tri-State District.—Of the major zinc-lead mining fields in the Mississippi Valley, the Tri-State District of Missouri-Kansas-Oklahoma had had the most intensive investigation prior to 1939. Numerous works by Siebenthal (2), Fowler and Lyden (3, 4, 5) and many others have described the stratigraphy and structural setting of the ore bodies in great detail.

Since 1939, the U. S. Geological Survey has published detailed maps and geological descriptions of many of the deposits—the results of an extended program directed by McKnight (6). The contour maps of the Picher, Oklahoma area, showing the structures on the various producing horizons are the first published compilations of these data for the whole field, although similar maps have been used by geologists working for the various mining companies. In 1943 the Missouri Geological Survey produced a set of maps (7) of the Missouri part of the district showing areas mined on different stratigraphic levels and the distribution of Pennsylvanian shale remnants, there being a marked correlation between ore in certain beds of Mississippian limestone and slumped shale pockets.

In 1950 Lyden (8) summarized the geological interpretation of the ore deposits, offering some information additional to that in his earlier works with Fowler, and discussing the application of geology to exploration and mining.

An investigation of the direction of flow of the ore solution as indicated by asymmetric growths of minerals in the many cavities and open channels was reported by Stoiber (9) in 1946.

Wisconsin-Illinois District.—An immense amount of detailed geologic investigation has added to the knowledge of this district since the publication of Special Paper 24. The U. S. Geological Survey, the Illinois Geological Survey and the U. S. Bureau of Mines have published many broad regional descriptions as well as detailed studies of individual mines so that the literature is more complete for this area than for any other. A good bibliography may be found in Agnew's A.I.M.E. Tech. Paper 40451 (10). An interesting interpretation of the ore-controlling structures recently has been given by Reynolds (11). The revival of mining interest and production from this field is in no small way the result of these extensive geological programs.

Southern Illinois-Kentucky Fluorspar-Zinc-Lead District.—This district was not included in Special Paper 24, probably because the predominately

fluorspar mineralogy and the fissure vein type of ore occurrence seemed to put these ores in a different category from the other deposits of the mid-continent region. Since the publication of Special Paper 24, however, very large and important limestone replacement ore bodies have been found near Cave in Rock, Illinois, and Carrsville, Kentucky, and these have many features in common with the more "normal" Mississippi Valley group. The importance of these bedded ores was not recognized prior to 1938. Fluorspar is still the predominant ore mineral but galena and especially sphalerite are abundant. The papers by Grogan (12), and Weller, Grogan and Tippie (13), as well as the map of the Kentucky part of the district by Weller and Sutton (14) are valuable additions to the earlier works by Bastin (15) and Currier (16, 17).

The question as to whether to include these deposits in this discussion arose early in the preparation of the paper. In order to determine the concensus of professional opinion, a mail canvas was made of a group of geologists, many of whom had worked in the fluorspar district or other of the Mississippi Valley areas. The overwhelming opinion (27 to 5, with 9 abstaining) thought the Illinois-Kentucky ore was closely akin to the ore in southeast Missouri, Joplin and elsewhere, and therefore the inclusion here seems justified (or at least popular).

Southeast Missouri Lead District.—Geologic understanding of the lead deposits in southeast Missouri has advanced greatly since the inauguration by St. Joseph Lead Company in 1947 of its detailed study guided by John S. Brown. A number of publications have resulted (18, 19, 20, 21). In the Fredericktown, Mo. part of the district, the National Lead Company has also been active geologically, but to date their results have not been published in detail. The Missouri Geological Survey has published results of a stratigraphic study by James of the ore formation in the Fredericktown area (22), and James has described separately the broad structural associations of the mineralization in the entire district (23).

From these papers it is evident that the southeast Missouri lead deposits represent an outstanding example of close relationship between ore and sedimentary depositional features such as lime sand banks, algal reefs and facies changes. Some of this information is significant insofar as the problem of the origin and nature of the ore fluid is concerned.

A special study of the clay minerals associated with the ore was made by Beaumont (24) and the Geological Society of America, Lamont Laboratory and the St. Joseph Lead Company have cooperated in a joint study of the distribution of lead isotopes in the district (25). An interesting paper by Frederickson (26) ascribes the deposits to processes of sedimentation, diagenesis, and recrystallization with concentration on the clay minerals by base exchange.

Appalachian Zinc, Lead and Barite Province.—The zinc, zinc-lead and barite deposits of the Valley and Ridge province of eastern United States were not included in Special Paper 24, but, since most geologists who are familiar with the area regard them as examples of the Mississippi Valley type, evidence from this field should be included in discussions of origin. The

province extends from Alabama to Pennsylvania with important deposits at Mascot, Jefferson City, and Treadway, Tennessee; Austinville and Timberville, Virginia; and Friedensville, Pennsylvania. Most of the ore is lead-free but at Austinville, there is a substantial lead production. Most of the mining is in the Kingsport formation of Beekmantown age, but the Austinville ore is in the Cambrian Shady formation. The largest number of the deposits over this tremendous area, 750 miles long, have so many features in common (i.e., lack of nearby igneous rocks, light colored sphalerite, no lead, occurrence as fracture fillings in brecciated fine grained dolomite or as dissemination in coarse crystalline dolomite) that they must be considered as members of the same family.

This district has been the object of an intense geologic study in the past 15 years and tremendous reserves have been found that give the area the greatest known zinc potential in the United States. Beginning with the detailed mapping of the late Josiah Bridge in the 1930's, the U. S. Geological Survey, the several state surveys, and numerous private companies have enlarged the geologic knowledge of the occurrences. Several important publications have appeared, notably those of Oder and Miller (27), Oder and Hook (28), Herbert and Young (29), Crawford (30), and Brokaw (31). A U.S.G.S. publication on the East Tennessee deposits by Brokaw is under preparation (32). Bridge's map and the accompanying text, edited by Rodgers (33), are basic information for the Tennessee part of the province. It is to be hoped that at some future date much of the very interesting but presently confidential information about the structural and stratigraphic relations, mineral zoning, alteration halos and rare metal relationships will be published.

The barite deposits around Sweetwater, Tennessee described by Dunlap (34) and Laurence (35) occur in a geologic setting similar to the zinc deposits and must be related to them genetically.

Other Districts in the United States.—Vein or bedded deposits of the Mississippi Valley type occur in many places, especially in the mid-continent region. Most of these were the objects of investigations during World War II. Often drilling was done either by the Federal government or by private companies. Reports of the Federal government activities in most of the areas have been published in the Reports of Investigations series of the Bureau of Mines. These reports are not intended as complete geologic descriptions but they do describe the general relations of the deposits and serve to demonstrate the widespread distribution of this type of ore. Included in this group are the Central Missouri zinc-barite-lead district, the North Arkansas zinc-lead district, and the Central Kentucky-Tennessee barite-lead-zinc veins. E. T. McKnight's 1935 U.S.G.S. Bulletin 853 is still the recognized authority on the North Arkansas district.

The interesting lead deposits of the Llano uplift area in Texas have been described recently by Barnes (36). These are remarkably similar in geologic setting to the ores in southeast Missouri.

The zinc deposits in the Arbuckle formation near Davis, Oklahoma have studied and drilled by a private company, but there are no new publications describing them. The mineralization itself is somewhat like that in East

Tennessee, but the structural setting of the ore-bearing outcrops with the Arbuckle dipping away from resurrected Precambrian igneous knobs is more like that in southeast Missouri. A few hundred miles to the north of Davis, in Central Kansas, zinc sulphide has been noted in oil wells in this same stratigraphic horizon at a depth of over 5,000 feet (37).

In many respects the ore at Metalline Falls, Washington, and northward into British Columbia resembles the deposits in the Mississippi Valley, and some geologists regard it as belonging to this group. In 1936 the U. S. Geological Survey instituted a study of the Metalline Quadrangle which was intensified during World War II. The first product of this effort is Prof. Paper 202 by Park and Cannon (38). Mills described the geology of the various mines before the A.I.M.E. in 1954. A new publication by the U. S. Geological Survey is in press (39).

Districts Outside the United States.—There are many important zinc and lead producing areas of the Mississippi Valley type outside the United States. Perhaps the most important one in North America is at Pine Point in Northwest Territories, Canada. Only general geologic descriptions have yet been published on this ore occurrence (40). No mining has been done but in the past ten years prospecting of the deposit has shown an immense potential. The ore occurs in Devonian limestone on the south shore of Great Slave Lake.

Another much smaller Mississippi Valley type district is in British Columbia where the Monarch and Kicking Horse mines yielded lead and zinc from Cambrian limestone and dolomite. The geology of this area has been described by Goranson (41).

In North Africa a lead-zinc province of major proportions extends from Morrocco east-northeastward through Algeria and Tunisia. Large ore bodies found in recent years near the Morrocco-Algeria border will support increasingly large production in the future. The ore replaces Jurassic limestone and, in mineralogy and structure, is similar to many other districts of the Mississippi Valley type.

A number of publications report the results of recent studies in this large area. Several of them are in English, notably those of Claveau, Paulhac and Pellerin (42) on the new Morroccan deposits and that by Sainfeld (43) on Tunisia. The theory of origin outlined by Schneiderhöhn (translated by J. S. Brown) (44) likewise is a valuable contribution in that it elucidates an hypothesis of ore genesis more widely held in Europe than in the United States.

The great lead-zinc deposits of Belgium, Luxemburg, Germany and Poland have been highly productive for such a long period that the ore we call the "Mississippi Valley type" could just as properly be termed the "Central European type." Unfortunately, most of the published descriptions are in journals not widely available in the United States. Zwierzycki's description (45) of the Polish deposits and de Colbertado's paper (46) on Raible, in the 16th International Geological Congress symposium report, are, therefore, especially welcome. They propose a "telemagmatic" origin whereas many of the earlier authors had advocated genesis by "lateral secretion" or "re-

juvenation." C. H. Behre, who has long been a student of Mississippi Valley deposits, has drawn comparisons between the North American ores and features noted in visits to the European localities (47).

No new geologic descriptions of the once-very-productive deposits of the Moresnet district in Belgium and Luxemburg have appeared in recent years. The sphalerite and galena replace Devonian-Carboniferous limestones near large faults. There is now little production from the area. Not far away, near Duren in West Germany, however, production of lead with some zinc from Triassic red sandstone and conglomerate has been revived since World War II. The deposit, known as Maubacker-Bleiberg, is similar to the famous Mechernick ore body that is close by. Descriptions of these interesting deposits have been given by Fritsche (48) and Behrend (49).

Great Britain has many important deposits of this type that have been mined for several hundred years. Important contributions to the literature have been made in recent years by Traill (50), Dunham (51), Schnellmann and Willson (52), and Shirley and Horsfield (53).

In addition to the above cited descriptions of specific mines or districts, a considerable amount of data on Mississippi Valley type ore deposits is to be found in general discussions of geologic principles and processes which have been investigated on an intensified scale in recent years.

CHARACTERISTICS OF THE DEPOSITS

These deposits have a number of characteristics that differentiate them as a group. Although not all of the ores from the different districts exhibit all of the characteristics, there are present invariably enough of the typical features so that most geologists quickly identify each area as a representative of the Mississippi Valley type.

Absence of Igneous Rocks that are Potential Sources of the Ore Solutions.—The one universal and fundamental characteristic shown by all of these deposits is a lack of nearby bodies of igneous rock that are obvious or even likely sources of the ore solutions. In several of the districts (as Southeast Missouri and Rosiclaire) there are basic dikes but there is no evidence that the dikes and ore are related. The district with the closest granitic rock of a suitable age is Metalline, but even here the distance between the ore bodies and the intrusives as exposed on the surface is several miles and there are no features in either the granite or the ore deposits that suggest a kinship. Most of the districts have no evidence whatever of igneous activity that is younger than the ore host rock. This characteristic of Mississippi Valley type ore, of course, is the one that has confounded the hydrothermal school.

Simple Mineralogy.—The mineralogy of each of the districts is quite simple but, when all of them are considered as a group, quite a surprisingly long list of minerals and elements is found to be represented. Galena, sphalerite, barite and fluorspar are the main ore minerals but there is subordinate production of copper, cadmium, indium, germanium, gallium, cobalt, nickel, silver, iron and sulfur. The principal copper mineral is chalcopyrite; cobalt and nickel occur in siegenite in southeast Missouri. Sphalerite concentrates,

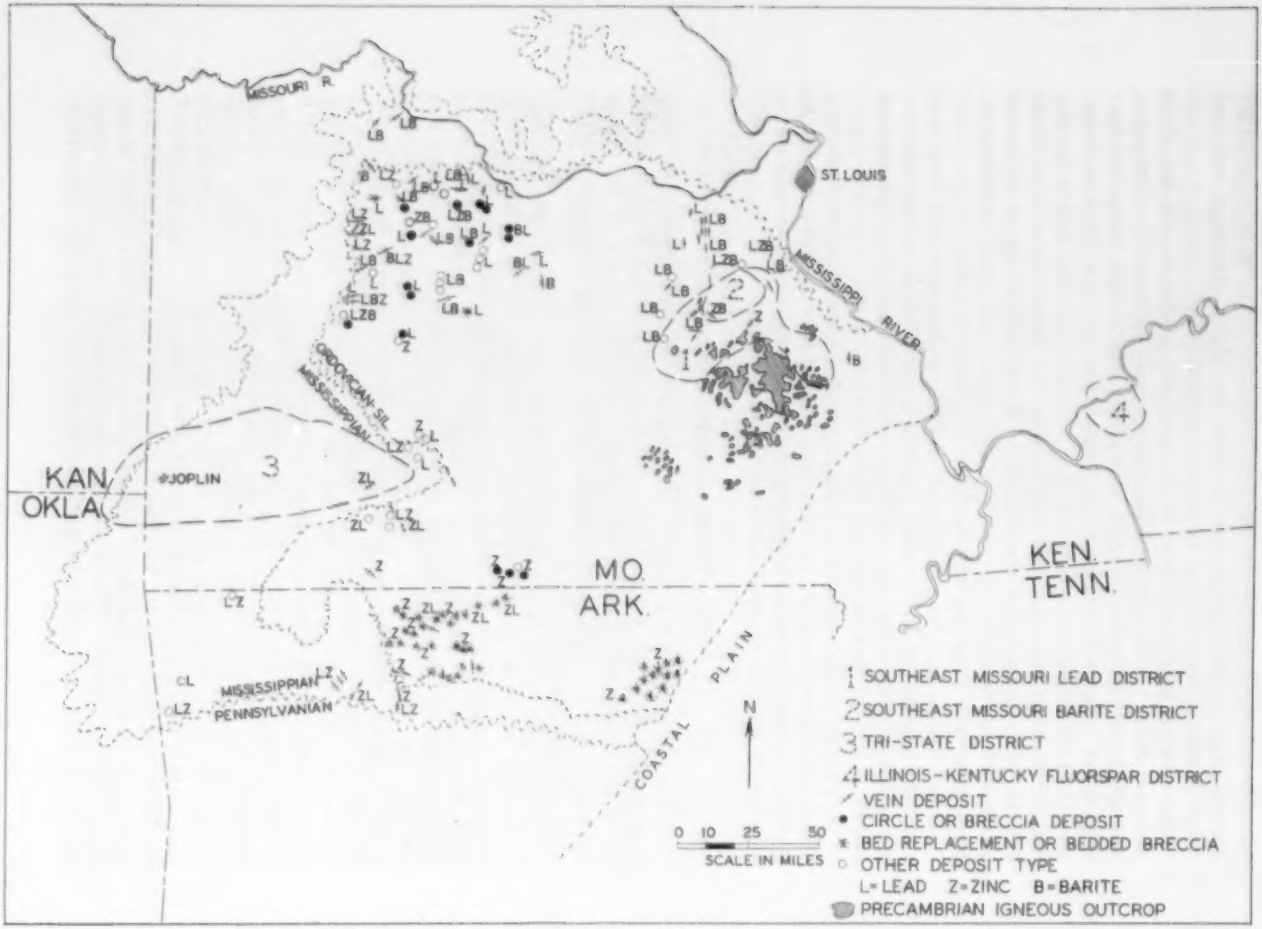

FIG. 2. Distribution of ore mineral showings and orebody types in the Ozark region.

largely from these districts, are the world's principal source of cadmium, indium, germanium and gallium. Greenockite is not uncommon but no indium, germanium or gallium minerals have been identified and it is probable that all four elements for the most part are simply non-essential constituents of the sphalerite. Iron and sulfur, in the minerals pyrite and marcasite, in places are sufficiently abundant to be concentrated and shipped to sulphuric acid plants. Occasionally "unusual" minerals are reported such as jordanite, gratonite, and meneghinite in Silesia and enargite in Joplin and North Arkansas.

Each district has its own characteristic mineral assemblage and this may contrast quite sharply with that of its nearest neighbors. The situation around the Ozark Dome is particularly striking in this regard, as shown in Figure 2. Around the periphery of this structure, which has a major axis about 350 miles long, there are at least five entirely different ore mineral groups. These are in the Southeast Missouri, Tri-State, Central Missouri, North Arkansas and Washington County (Mo.) districts. Each has its own characteristic alteration type, favorable structural habitat, and paragenetic sequence. Each occurs at a different stratigraphic horizon but each is unmistakably a member of the Mississippi Valley type.

The minerals listed above occur both as replacements of country rock and as open space fillings. The latter type of occurrence, particularly in the Tri-State district, has provided many of the spectacularly large crystals of these minerals seen in museums.

The gangue mineralogy likewise is simple. Dolomite, calcite, jasperoid, chert and quartz virtually comprise the list. Adularia rarely is noted.

Wall rock alteration is simple in mineralogy also, but commonly the effects are quite pervasive. The main processes are dolomitization, chertification and recrystallization of the carbonate minerals. In some districts there is so little alteration that it seems as though the introduction of the ore minerals themselves was the only effect. Where the ore minerals have a widespread distribution it is difficult to separate even wider spread alteration effects from regional sedimentation features.

A distinctive feature of the mineral composition of Mississippi Valley ores, first noted by Nier in 1938, is the anomalous lead isotope percentages that characterize the galenas from this area. There is an abnormally high content of radiogenic lead. Not all deposits of the ore type have been tested and no completely satisfying explanation of the observed situation has been presented, but it would appear that the unusual and distinctive isotopic composition may prove to be another of the "peculiarities" of a Mississippi Valley type of ore deposit.

Low Precious Metal Content.—In contrast with lead ores formed under more intense conditions, Mississippi Valley deposits contain very small amounts of silver and practically no gold. Lead concentrates from southeast Missouri, for example, assay one ounce of silver per ton which is about average for the group. Surprisingly, southeast Missouri zinc concentrates contain about 20 ounces of silver per ton. No separate silver minerals have

been identified and it is probable that the silver simply constitutes an impurity in the galena and sphalerite.

Occurrence in Limestone or Dolomite.—Most of this ore is found in rock that is or was at one time limestone or dolomite. However, there are certain notable exceptions that indicate that a carbonate host is not essential. At the Hayden Creek Mine in southeast Missouri galena favors a pile of granite boulders in preference to the Bonneterre dolomite which is the main ore carrier over most of the district and is available immediately overlying the mineralized boulders. It is true that the preponderance of the galena replaces the sandy dolomitic matrix between the boulders but a substantial fraction is found in veins within cracked granite blocks.

Likewise in the Southeast Missouri district, at the No. 8 Mitchell Mine and at Mine Lamotte, lead is produced in large amounts from sandstone at the base of the Bonneterre and in the top of the Lamotte formation. The galena occurs both as cementing material filling in between sand grains and as a replacement of pre-existing dolomite cement. The Maubacker-Bleiberg ore of West Germany has a similar occurrence, in sandstone red beds.

The age of the host rocks has a wide variation—ranging from Upper Cambrian to Jurassic. Most of the deposits are found in Paleozoic formations.

Bedded Replacements and Veins.—Most of the tonnage of Mississippi Valley type ore has come from bedded replacement deposits and in these the ore of each district shows great selectivity for certain favorable beds. A smaller but still important production has come from veins such as those in Central Kentucky and Tennessee, in England and in the Illinois-Kentucky fluorspar district. The "pitches" of the Wisconsin-Illinois field likewise are cross-cutting and veinlike. Ore bodies of various sizes have been found in what are almost pipe-like brecciated structures. The Oronogo Mine, north of Webb City, Mo., the Alice Mine, near Caulfield, Mo. and the interesting Bowers-Campbell ore body near Timberville, Va. are but three of many that might be mentioned. Many of the cross-cutting brecciated structures that are nearly round in plan seem to be related to solution slumps and sink holes.

Most Common Location in Passive Structural Regions.—For the most part Mississippi Valley type ore deposits are located in regions that have not undergone strong mountain building activity since the ore-bearing beds were deposited. The mid-continent area of North America, extending from central United States northward through the plains province of Canada, and the central European region are the outstanding examples.

This is not to imply, however, that none of the districts lie in areas that have been affected by orogeny. The Appalachian province is an area of tremendous overthrusting, and Raibl and the Metalline districts are much folded and faulted. Swarms of faults, mostly normal, cross the Illinois-Kentucky field and, in fact, most of the large veins occupy faults. Faults likewise are prominent in and around the north African province.

Shallow Depth.—For many years it was postulated that ores of the Mississippi Valley type would only be found near the surface and it is true that

virtually all of the production to date has come from depths of less than 1,000 feet. This, however, could possibly be due to the fact that the ore bodies at or near the surface quite naturally were the first ones found. Then, due to the gentle dips in most areas, the workings did not extend to great depths.

New discoveries in the past twenty years, however, have challenged this old axiom. Ore is now known to exist at 1,500 feet in Missouri and some of the great new finds in Tennessee are over 2,000 feet below the surface. If the zinc noted in the oil wells in central Kansas represent ore of the Mississippi Valley type, as is not unlikely, then the depth range exceeds 5,000 feet. It seems probable that within limits the depth at which ore exists is governed principally by the depth at which the favorable formation exists.

Relation to Positive Structures.—In quite a few of the districts there is a definite tendency for the ore to occur in structurally positive areas. The structures themselves have many diverse origins, some of them being original sedimentary features and others being the result of folding or faulting. In southeast Missouri considerable ore is located over and along the flanks of "knob" structures in which the favorable beds show initial dips away from Precambrian highs (18, Fig. 4, p. 213). The same is true in the Llano area of Texas. Not uncommonly in Missouri, the "knob" structure has been accentuated by algal reefs that grew on top of the igneous islands as submergence and sedimentation proceeded. Dips of 20 to 40 degrees in off-reef beds are common and the mineralization also especially favors this type of positive structure.

Still another example of positive structure ore concentration in southeast Missouri is to be found in the sedimentary depositional arches that localized the ore in the Flat River area (18, Figs. 6, 7, p. 216, 217). In lower Bonneterre time great banks of calcareous sand stretched out from the main St. Francois Mt. high in a northeast direction. As sedimentation proceeded these banks were buried by layers that draped over them in antiform structures. About a dozen of these structures have accounted for many tens of millions of tons of ore and practically all of the "upper level" ore (which lies from 100–200 feet above the Lamotte sand) is directly related to arches in the underlying beds. In considerable part this is due to the fact that algal reefs selectively grew in the shallow water on tops of the banks, and the long, northeast-trending reefs contained many loci later favored for ore deposition.

In the Valley and Ridge province of East Tennessee and Virginia the formations are tilted, and intensely folded and faulted. Dips from 10 to 50 degrees or even steeper are the rule. Tremendous overthrusts have pushed from the southeast and the favorable Kingsport formation outcrops in a series of northeast-trending belts. The major mineralization is in places where the strike varies from the normal and many of the better mines are on top of or on the flanks of positive structures. The belt from Mascot to Jefferson City, Tennessee (Fig. 3), is a particularly good example as the Grasselli, Universal, Jarnagin and Athletic Mines are on the flanks of the Cherokee anticline and the great new Young Mine is associated with Hodges Dome. On a smaller scale, many individual stopes are related to small anticlines and

domes as described by Brokaw and Jones (54). These positive structures in many places have been modified by solution and collapse, as described in the next section.

On a regional scale, the locations of various mineralized districts around the Ozark Dome, the Wisconsin Dome, the Arbuckle Mts. and the Llano Mts. appear to be evidence for ore control by positive structures, and indeed they may be. It must be considered a possibility, however, that this apparent localization may be simply the result of the fact that they are areas of outcrop of the favorable beds where ore bodies were more easily discovered.

The close relationship of the ore bodies in many districts to positive structures strongly suggests that any solutions active in ore deposition were rising

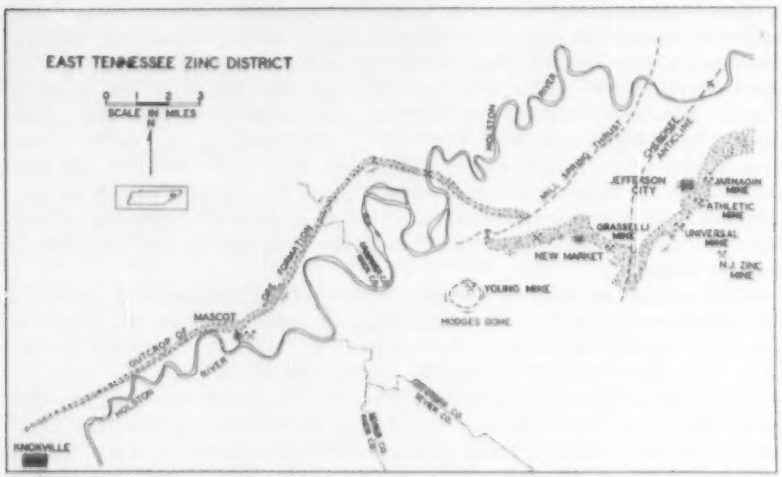

FIG. 3. Distribution of the zinc mines and the ore formation outcrop in the Mascot-Jefferson City belt of eastern Tennessee. Note the concentration of ore deposits on the flanks of the positive structures.

rather than descending. Indeed, in southeast Missouri the pattern of the arch-type ore bodies and the dolomitization of surrounding limestone, especially as seen in cross section, virtually precludes the possibility that the ore solutions there could have been descending.

Evidence of Solution Activity.—A number of these deposits show evidence of solution preceding deposition of the ore minerals. In some instances the solution, generally with accompanying collapse, seems to have occurred simultaneously with ore fluid circulation and must have been accomplished by it. Thus the ore fluid not only brought in the metallic minerals but actually participated in ground preparation.

In southern Illinois, Grogan (12) has described with careful documentation the dissolution of the Fredonia and Renault limestones and the resulting

collapse of the overlying Rosiclare and Bethel sandstones. Fluorspar, sphalerite and galena, along with gangue calcite, encrust the collapse breccia fragments (12, Figs. 2, 6). Some of the reduction in volume is attributed to replacement of rock calcite by fluorite, which has a stoichiometrically smaller volume. Thus the dissolution, the replacement by ore mineral, the collapse and the encrusting of the fragments all occurred in close sequence if not actually simultaneously.

In the Wisconsin-Illinois district thinning of the "glass rock" and "oil rock" zones almost always accompany major mineralized trends in the overlying cherty dolomites. The high angle "pitch" structures, in which the ore fills fractures extending at high angles across several tens of feet of beds, in

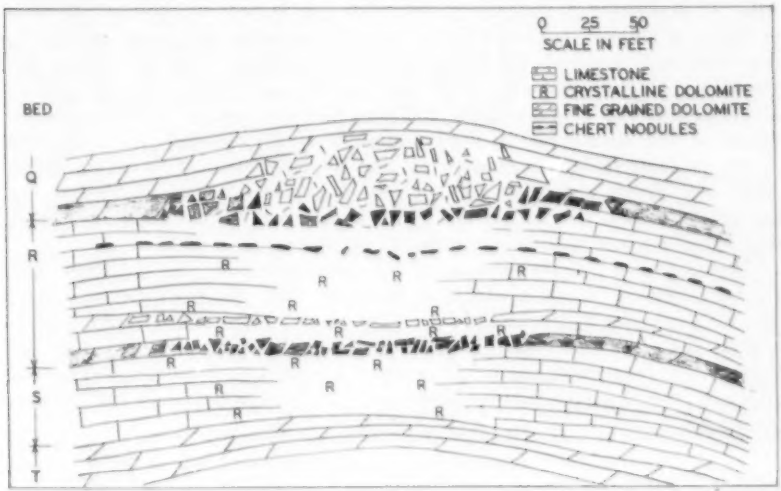

FIG. 4. Partially schematic cross section of an anticlinal ore trend in which the structure has been modified by solution action. East Tennessee zinc district.

some cases have been shown to be results of collapse as the "oil rock"-"glass rock" zone was thinned from an average thickness of 30 feet to 10 feet or less (11, Figs. 12, 13).

In East Tennessee the stratigraphic section of the mineralized zone is so constant and so many beds have distinctive appearances that there is an unusual opportunity to study and measure offsets. Brecciation of brittle dolomite beds is a prominent feature of all of the deposits, but even in severely jumbled piles of blocks it usually is possible to state with certainty the exact stratigraphic level from which most of the blocks have come (Fig. 4). Here, then, is an exceptional chance to study just what has happened in the brecciation process.

For many years there was strong disagreement as to the mode of origin

of this breccia and probably not all geologists are yet in complete accord on all the details of the process. Studies of the past ten years, however, have shown that thinning of interbedded limestone zones always accompanies the breccia and that the "founder breccia" explanation originally proposed by Ulrich (55) and more recently advocated by Oder, Hook and Odell (28) is correct. Regional stress probably contributed to the collapse of solution-induced openings, but the presence of the openings was necessary for the creation of any sizeable body of breccia. Fragment by fragment study has shown that almost without exception the blocks are below rather than above their original structural position. Some have dropped several tens of feet.

A striking characteristic of these tremendous masses of broken blocks is the dearth of open space now. The inter-block voids were almost completely filled by deposition of gangue dolomite and sphalerite. Apparently the mineralizing solutions circulated under enough pressure and long enough to penetrate and completely fill the narrowest of openings. The brecciation and fracturing die out gradually in the walls of the ore bodies, not abruptly as would be expected if cave collapse had been the only process. The impression gained is that the solution of the limestone beds, the collapse of the dolomite layers, possibly under regional stress, and the circulation of the ore solution were very closely spaced in time. If the dissolution can be ascribed to the ore solution itself as Grogan has done in the case of the southern Illinois deposits, the whole process was virtually simultaneous.

Solution and collapse structures are mineralized in the Tri-State and Central Missouri districts. In both, however, the ore structures are much like the sink holes and collapsed caves that are a feature of the Ozark region, and no distinctive difference between those that have ore and those that are barren have been recognized. It is not impossible to visualize pre-existing sink and cave structures having been reactivated and enlarged by ore solution circulation.

ORIGIN OF THE DEPOSITS

If it is admitted that the enumerated deposits have so much in common that a common mode of origin is likely, it is obvious that this mode of origin must be a flexible scheme capable of fitting into all the observed patterns and explaining all the variations from district to district. It must give a logical explanation for the presence of great lead ore bodies on one side of the Ozarks and equally great zinc ore bodies on the other side; it must account for the veins and the bedded ores, for replacement and open space filling, and for extensions to depths of several thousand feet below the surface. And further, it must account for the great lateral distances that are involved.

There are at least five modes of origin for which substantial arguments have been advanced in one or more districts:

1. Original deposition.
2. Original scattered deposition with modification by regional metamorphism.

3. Original scattered deposition with modification by circulating ground water moving up.
4. Original scattered deposition with modification by circulating ground water moving down.
5. Deposition from fluids of igneous derivation with hydrothermal or gas transport either with volatile aid or simply as metallic vapor.

These will be discussed in the order listed.

1. The theory of original sulphide deposition as an extraordinary sedimentary process has been advocated especially in recent years for the copper deposits in Rhodesia (56) and at White Pine, Michigan (57). Much earlier the proposal was made for the Kupferschiefer in Germany. This hypothesis obviously cannot apply to any of the veins or to any of the deposits related to faults or other secondary structures as many of the Mississippi Valley deposits are. There is also considerable doubt as to whether such an origin is possible for the beds of solid galena and sphalerite several inches thick such as have been mined in Southeast Missouri and the Tri-State district. Hence this scheme may be dismissed from serious consideration as an explanation of the Mississippi Valley type of ore deposit.

2. The second of the genetic proposals listed, original deposition modified by later metamorphism, is the one advanced by Schneiderhöhn (44). As he visualizes the mechanism, the distribution of atoms in nature is largely determined by environment and a sufficiently intense change in the environment of a deposit may set the atoms in motion. They will move to a new location where they are again stable. This may be repeated many times during successive orogenies. The idea was first developed in connection with certain Alpine deposits, but in his latest paper was proposed for the north African lead-zinc field. For the African area it is postulated that lead-zinc concentrations in the paleozoic basement rocks, quite probably of sub-commercial grade, were set in motion by the Alpine orogeny and came to rest as ore grade replacements of the Lias dolomite.

As Dr. John Brown states in the introduction to his translation of Schneiderhöhn's original work, the theory may be supported by evidence in the intensely deformed Alpine mountain chain; it might possibly be accepted for north Africa though with less conviction; but in the Mississippi Valley there simply has been too little regional metamorphism for the idea to gain much backing. It would be necessary to have deposits in the Precambrian rocks that were the source of lead and zinc in the "regenerated" ores. No such potential source has been found in the many square miles of exposed Precambrian granite and porphyry in southeast Missouri and none has been found in drill holes. The idea, thus, breaks down if an attempt is made to apply it to Mississippi Valley type deposits generally.

An hypothesis of metal concentration somewhat similar to Schneiderhöhn's but not requiring strong regional metamorphic action was proposed by Frederickson (26) for southeast Missouri. It relied on the surface chemistry of clay minerals as the collecting force. An original sparsely distributed metal content would, during several periods of mobility, be concentrated due

to the attraction of metal ions to grains of clay, which are not uncommonly associated with lead ore on the lower levels of the Southeast Missouri district. Here again is an hypothesis designed to explain a specific ore type. Much ore is associated with black shale bands in southeast Missouri; also in the "flats" of the Wisconsin-Illinois district where limestone solution has been advocated. But the theory does not explain the millions of tons of southeast Missouri ore not associated with clay concentrations; nor could it seriously be proposed for the Wisconsin-Illinois "pitches," the Appalachian zinc deposits or the many vein ore bodies in the southern Illinois-Kentucky, Tennessee, or English districts. Clay minerals may exert an influence on the localization of certain ore bodies but they are not the explanation for most of the ore concentrations.

3–4. The third and fourth genetic alternatives involving ground water are essentially the same process but one invokes artesian circulation and the other simply downward percolating or laterally moving ground water. The original deposition of the metals was during more or less normal sedimentation, with the lead, zinc, and other ore components being highly dispersed. According to the theory these widely scattered bits of metal were gathered up by leaching from the rock and concentrated by re-deposition in favored reservoirs or host rocks.

The artesian hypothesis has been advanced especially for the Tri-State and Wisconsin-Illinois districts. In both instances the deposits are on the flanks of great domal structures and artesian circulation does exist. No such circulation exists in southeast Missouri where sizeable faults have reversed the regional dip in the main ore-bearing block and have cut up the area in such a way as to reduce greatly the size of the potential metal "gathering ground". Artesian conditions do not exist and may never have existed in several of the important areas under consideration. Yet, in some of these districts, as noted before, there is structural evidence that indicates that the ore solution was rising rather than descending.

A number of serious objections have been raised that question the ability of this hypothesis to account for even the Joplin and Wisconsin-Illinois deposits. For example, how efficient is ground water in completely leaching metals out of a large block of limestone? The walls of solution channels are leached for a short distance admittedly, but in most cases the limit of the leaching is marked by an obvious color change. Much rock shows no evidence of leaching. If large bodies of rock cannot be penetrated by solution to remove the metal, is not the supply of available metal too limited to give rise to an ore body, even if one grants complete efficiency in later deposition?

Other objections involve the causes of precipitation of the metal from ground water. In some places carbonaceous material has been called upon; in other places there is no carbonaceous matter but ore is present.

Still further doubts arise when the Mississippi Valley type deposits are considered as a whole. Can one really believe that lead- or zinc-bearing ground waters circulated at depths in excess of 1,500 feet in southeast Missouri, or over 2,000 feet in east Tennessee? If so, such ground water conditions

have not been suggested by any other line of evidence. This question also arises in regard to the zinc showings in the Arbuckle of Central Kansas at 5,000 feet below the present surface.

Despite these questions that must be answered by supporters of the meteoric water hypotheses, the theories cannot be rejected from further consideration. Much has been learned in recent years as to the chemical capabilities of ground water as well as of hypogene solutions. Our knowledge of geochemistry in general and especially of the stability ranges of various elements is becoming much more precise. The tremendous amount of research on uranium and vanadium ores of the Colorado Plateau indicates what can be accomplished by a concerted effort. A similar effort on the Mississippi Valley lead-zinc-barite-fluorspar ores undoubtedly would improve our understanding of them.

In connection with the Colorado Plateau deposits, over which the same syngenetic-epigenetic, hypogene-supergene argument rages, the recent emphasis by George Bain (58) on the distinction between "hydrothermal" and "hypogene" is significant. Bain's point is that heated meteoric water is "hydrothermal" (but not hypogene) and might accomplish similar-looking effects to those caused by a true hypogene solution. Hence it might work over and redistribute syngenetic concentrations so that they had all the earmarks of true hypogene deposits. They would not be hypogene deposits, however, because the active solution had not carried the metals from their original source to the sites of deposition. The distinction becomes a delicate one because a much cooled hypogene solution a long way from its source and possibly somewhat contaminated with normal ground water might be difficult to tell from slightly warmed ground water—even if one was there to watch the flow go by and not just observing the effects of such flow.

5. The fifth and last of the major hypotheses that has been advanced to explain the Mississippi Valley type ores is the well known "Hydrothermal Theory"—or to acknowledge Dr. Bain's distinction, perhaps better called the "Hypogene Hydrothermal Theory." Possibly an even better designation would be "Deposition related to igneous activity" since one should include versions of the theory calling on metallic vapors. All geologists are familiar with the many lines of evidence which show that emanations from magmas can give rise to ore deposits so the problem here is simply one of determining whether such emanations did give rise to the Mississippi Valley ores, and secondarily, what were the details of the process.

The hydrothermal theory has an advantage in its ready flexibility. It encounters no problem in explaining major zinc-minor lead deposits on one side of the Ozarks and major lead-minor zinc on the other side, with fluorspar-zinc two hundred miles farther east. Such variations are to be expected and are common in many western mining areas.

Likewise, the hypogene theory is not faced with serious limitations as to the pressure motivating circulation. Some of these ores are in rather tight rocks. Ground waters obtain their pressure only from the hydrostatic head, whereas igneous-derived circulation is pushed by potentially very high pressure

—the pressure that obtains being determined more by the resistance of the channelway than by the adequacy of the source. Whatever pressure is necessary to provide sufficient outward flow of the fluid is the pressure that will develop—new outlets will be found or created until the fluid production and escape are in balance.

The numerous structural, mineralogical and alteration variations from district to district likewise offer no problems of explanation. Veins, bedded replacements and breccia fillings; virtually unlimited combinations of mineral species; and dolomitization and silicification are all well known in districts of accepted hydrothermal origin.

Thus many problems that confront other theories are readily explained by the magmatic hypothesis. However, this question is not so simply decided as that. Aside from the complete absence of exposures of a likely parent igneous body, certain features of these deposits require some modification of thinking as to the hydrothermal mechanism.

Consider, for instance, the immense size of the areas involved in some of these districts. Either the ore solution circulated great distances or the solution source itself was very large. In Southeast Missouri, it is 50 miles from Fredericktown to Indian Creek; in the Tri-State it is over 100 miles from Springfield, Mo. to Miami, Okla.; and in the Appalachians, from Sweetwater, Tennessee to Friedensville, Pennsylvania is 600 miles, not continuously mineralized but at least in one ore-bearing province with very similar ore occurring in many places. In both the Southeast Missouri district and the Tri-State district there are at least 2,000 square miles in which, given the favorable formation, certain structures, and access to the mineral solutions, ore of a specific type may be found—not just similar ore but *identical* ore. The circulation problem and the probable size of the source magma body that is necessary are vastly different from those involved at Butte, or Bingham Canyon, or Cerro de Pasco. Here one must call upon a huge igneous mass emitting over its entire area mineralizers of amazing uniformity, or, with a smaller igneous source body, one must invoke circulation distances measured in tens, even hundreds of miles. It is this strain on the normal hydrothermal picture as advocated for deposits in western United States that raises a question whether in these Mississippi Valley types areas, if the ores are hydrothermal, there are not important differences in the process of ore formation. Such igneous rocks as are known in these regions are almost all basic, without acid counterparts; most of the areas are passive tectonically and there really is no direct evidence that magmatic differentiation has occurred in them. Is it possible that these emanations stem from a different kind of igneous source, more widespread in extent, which occurs at great depth and has no especial tendency to move upward to form intrusions? The low silver content and the anomalous lead isotope percentages in Mississippi Valley galenas as compared to ores of accepted hypogene origin suggests that these deposits, if they are hydrothermal, must indeed be a product of some variant from the simple hydrothermal family tree.

One characteristic of the southern Illinois and Appalachian ores gives a

clue as to the hydraulics of the ore solution circulation system. This is the tendency noted by Bastin (15), Oder and Hook (28) and others for late minerals to be deposited on the top sides of earlier formed minerals. In southern Illinois a crust of late calcite commonly is located exclusively on the top of earlier fluorspar (15, Fig. 27), and in east Tennessee the sphalerite location on rock fragments in the spectacular breccias has been compared to snow on a roof (28, Plate 1).

It is obvious that in these deposits the ore solution was not moving rapidly through its channelway and, indeed, at the time of deposition of the calcite and sphalerite, must have been essentially quiescent. Some sort of pulsating cycle in which the solution was replenished between periods of quiet crystal precipitation would be required by those advocating very dilute ore solutions. In the Tri-State district Stoiber (9) noted a definite irregular crystal growth pattern from which he could map directions of solution movement. But even here the rate of solution movement probably was slow, for Stoiber states (p. 39) that such evidence of vertical movement as he found shows downward settling. The gentleness of the Mississippi Valley ore-forming process is in marked contrast to the vigorous activity one associates with epithermal, mesothermal, and hypothermal deposits.

CONCLUSION

In summary, it is believed that the indications of kinship of the ore deposits of the Mississippi Valley type are so numerous and so demanding that it can be stated with considerable assurance that the basic mode of origin of all of them is the same. This paper has tried to show that many of the hypotheses that have been conceived to fit the facts in a single district are not acceptable when the limiting facts are taken from all the deposits as a group. The number of possibilities, thus, is reduced. If the next 18 years provide as much new information as has become available in the last 18, the answer to this 100-year-old problem may be obvious.

WHITE PINE, MICHIGAN,
November 17, 1958

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BRECCIA PIPES IN THE SHOSHONE RANGE, NEVADA[1]

OLCOTT GATES

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ABSTRACT

Near the crest of the Shoshone Range in north-central Nevada, three breccia pipes of Tertiary age cut deformed chert, quartzite, shale, and greenstone of Paleozoic age. The pipes average about 1 mile in longest dimension, have slightly flaring sides, and consist of the following units: (1) an outer discontinuous rim of coarse breccia of Paleozoic rock fragments; (2) an inner mass of fine-grained and much hydrothermally altered breccia that contains a thorough mixture of Paleozoic and Tertiary rock fragments and intrudes the marginal coarse breccia; (3) foundered blocks of Tertiary conglomerate and pyroclastic rocks intruded and engulfed by the fine breccia or younger rhyolite; (4) a more or less central plug of quartz monzonite porphyry or rhyolite that intrudes the fine breccia and the conglomerate or pyroclastics; (5) narrow flowbanded dikes of

[1] Publication authorized by the Director, U. S. Geological Survey.

rhyolite or quartz latite porphyry that cut all other rock types in the pipes and extend into the wall rocks.

The pipes were formed by an up-and-down pump action impelled by intermittent rise of the magma in the plugs. Brecciation occurred during upward movement of the magma and associated explosive volcanism. Breccia also was formed by subsidence, collapse stoping, and possibly rock-bursting during subsidence of the magma. The fine breccia thus formed ahead of the magma and, in turn, became intrusive, eventually working its way to or near the surface.

INTRODUCTION

THREE breccia pipes in the Shoshone Range, Nevada, were conduits during the Tertiary for a center of explosive volcanism. Excellent exposure by erosion, including sections 1,600 feet in depth, led to the hope that detailed mapping would give clues to the mechanism that formed the conduits and their breccia.

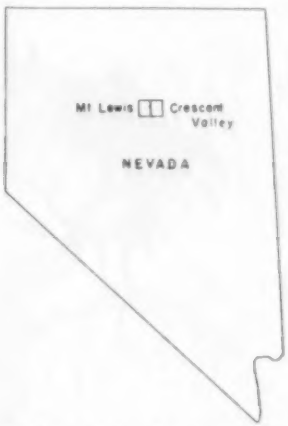
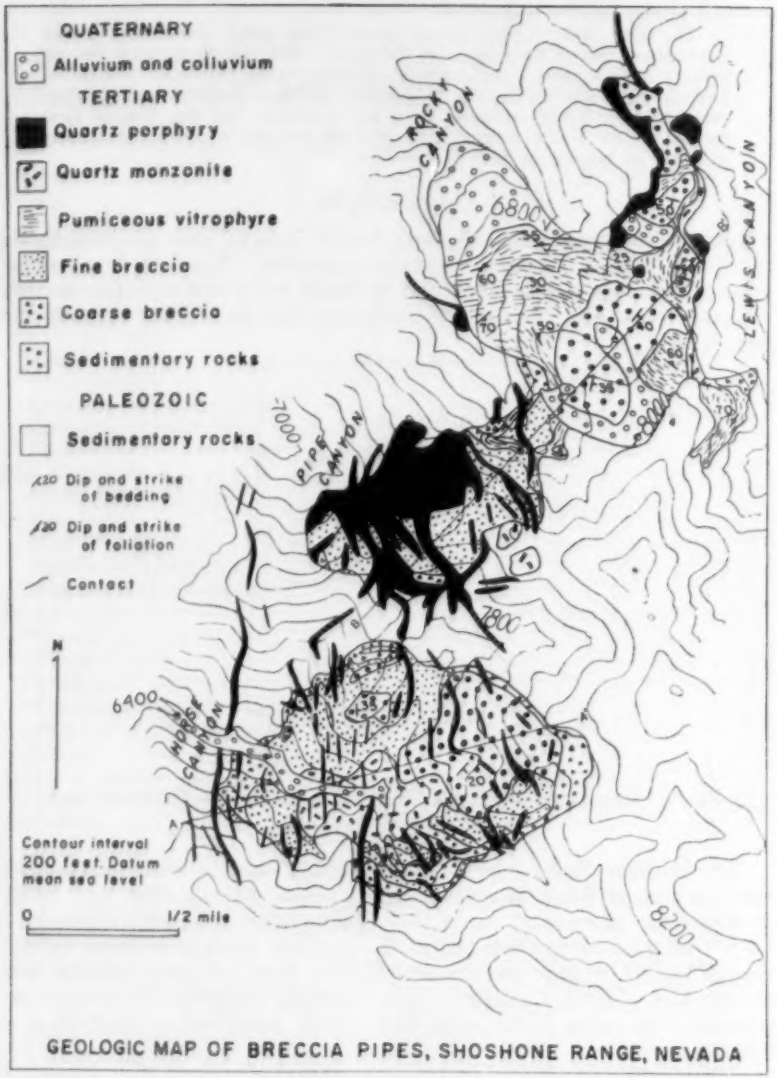


FIG. 1. Index map of Nevada showing location of the Mt. Lewis and Crescent Valley quadrangles.

The Shoshone Range is in the Mt. Lewis and Crescent Valley quadrangles near the town of Battle Mountain in north central Nevada (Fig. 1). Study of the breccia pipes grew out of the mapping of the two quadrangles by a U. S. Geological Survey field party. I am greatly indebted to James Gilluly, George Snyder, Harald Drewes, and Reuben Ross for many valuable field observations. Aaron C. Waters, Johns Hopkins University, gave much assistance in the study of the petrography of the rocks and in compilation of this report.

REGIONAL GEOLOGY

The breccia pipes are along the crest of the northern part of the Shoshone Range. The range begins southwest of Austin, Nevada, and trends slightly east of north to the Humboldt River. Crescent Valley lies to the east and



GEOLOGIC MAP OF BRECCIA PIPES, SHOSHONE RANGE, NEVADA

FIG. 2. Geologic map of three breccia pipes, Shoshone Range, Nevada.

the Reese River Valley to the west of this northern part. Maximum altitude is 9,680 feet at Mt. Lewis, about 5,000 feet above the floors of the neighboring valleys. The range is carved from a fault rock that was tilted eastward during late Tertiary time along normal faults on the west side. The northern part of the range consists primarily of Paleozoic sedimentary rocks intruded by the breccia pipes, by numerous dikes, and by several small stocks of Tertiary igneous rocks ranging in composition from quartz diorite to rhyolite. Late Tertiary tuff, welded tuff, agglomerate, and breccia and a few basalt flows have been spared from erosion on the flanks of the range and in a few fault blocks within it. It is probable that Tertiary volcanic rocks and conglomerate covered the site of the entire range prior to its uplift.

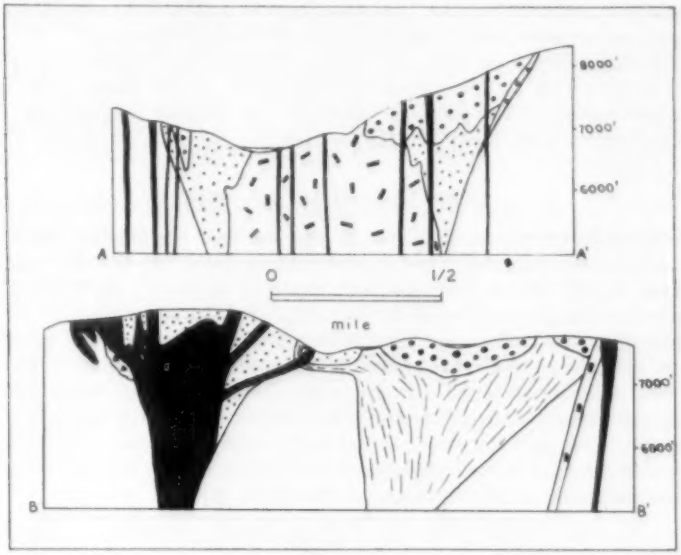


FIG. 3. Cross sections of the breccia pipes. Vertical and horizontal scales equal.

The Paleozoic rocks of the northern Shoshone Range are divided into two main units by the Roberts Mountains thrust, first mapped and described by Merriam and Anderson (13) in the Roberts Mountains about 40 miles to the southeast. The upper plate of the thrust consists primarily of Ordovician, Silurian, and Devonian chert, greenstone, quartzite, graywacke, arkose, argillite, and shale along with a subordinate amount of Carboniferous, Permian and Triassic limestone, shale and conglomerate. The lower plate consists of Cambrian, Ordovician, Silurian, Devonian and Mississippian quartzite, shale, limestone, and dolomite in stratigraphic units found within much of eastern Nevada and western Utah and well illustrated by the section at Eureka,

Nevada (14). The rocks of the lower plate are exposed in a few windows, the bulk of the exposed rocks of the range being of the upper plate.

The upper plate contains within itself at least ten thrust faults that can be traced for several miles and innumerable small ones that superimpose wedges and slices of rock on one another like a pile of shingles. In general these many thrust faults have low to moderate dips, but locally they are isoclinally folded and overturned. Dynamic or thermal metamorphism associated with the deformation has been slight. Maximum known vertical thickness of the deformed rocks of the lower plate exposed in the largest window is about 2,600 feet, with the base unexposed. The thickness of the upper plate is at least 10,000 feet and may be as much as 20,000.

The Tertiary volcanic rocks overlie those of Paleozoic and Triassic age along a profound unconformity, indicating a major episode or several episodes of uplift and erosion prior to the outbreak of Tertiary volcanism.

The three breccia pipes are strung out along a trend slightly east of north about a mile west of Mt. Lewis near the crest of the range (Fig. 2, 3). They are named (from south to north for the nearest canyon) the Horse Canyon breccia pipe, the Pipe Canyon breccia pipe, and the Rocky Canyon breccia pipe.

HORSE CANYON BRECCIA PIPE

General Description.—This breccia pipe lies near the head of Horse Canyon. It has an elliptical shape, slightly flaring sides, an east-west diameter of about 1 mile, and a north-south diameter of ¾ mile. Horse Creek and its tributaries expose a vertical section of about 1,600 feet.

The pipe cuts Ordovician chert, siliceous shale, quartzite, and greenstone except at the east end where it cuts Carboniferous limestone. The pipe crosses several thrust faults that dip gently east to northeast; the rocks composing the thrust plates, although highly contorted, generally dip in the same direction. The pipe thus cuts across both stratigraphy and structure, and neither its shape or its location appear to be controlled by either.

The following units were mapped within the pipe:

(1) An outer discontinuous rim of coarse breccia consisting of large blocks of the wall rocks.

(2) A fine breccia consisting of small fragments of many rock types that fills the central part of the pipe and intrudes the coarse breccia.

(3) Several foundered masses of Tertiary conglomerate surrounded and intruded by the fine breccia.

(4) A central plug of quartz monzonite porphyry that intrudes the fine breccia.

(5) Numerous dikes of quartz latite and rhyolite porphyry that intrude all the units outlined above.

(6) A few small dikes of hornblende andesite, the youngest rocks in the pipe.

Coarse Breccia.—Discontinuous patches of coarse breccia lie along the circumference of the pipe and project a few hundred yards into it. Coarse

breccia is best exposed on the topographic nose extending from the north wall (hereafter called the north nose) and on the south side of the south fork of Horse Creek.

Near the top of the topographic nose extending into the pipe from the east (hereafter called the east nose), the contact between the wall rock and coarse breccia is sharp but irregular. Along the north side of the pipe, the contact is also irregular but the wall rocks have been fractured to a distance ranging from 1 to 20 feet, without having been moved from their original positions.

The coarse breccia is a mixture of large and small fragments ranging from microscopic size to large blocks as much as 100 feet in length. Most of the large blocks are fractured; and all fragments, of whatever size, are angular, indicating that movement has been insufficient to round them.

The composition of the fragments of the coarse breccia reflects the lithology of the adjacent wall rocks. Where the wall rock is chert, the breccia consists primarily of chert fragments. Where the wall rock is limestone, the breccia fragments are of limestone. Admixture of rock types other than those in the adjacent wall rock is slight, and fragments of Tertiary porphyries are very scarce.

Some blocks of the coarse breccia have subsided into the pipe. On the north nose, large blocks of greenstone of a distinctive coarse ophitic texture lie 100 to 300 feet below the outcrop of the same kind of greenstone in the adjacent walls of the pipe. On the south side, the coarse breccia consists primarily of large blocks of siliceous shale, now opposite chert in the wall. The shale has subsided about 100 feet from its normal position above the chert.

The absence of size sorting, the angularity of the fragments and blocks, their obvious relation to the adjacent wall rocks, and the evidence of subsidence all suggest that landsliding and slumping of the margins of the pipe produced the coarse breccia. Furthermore, on the north and south sides of the pipe, fine breccia intrudes the coarse along curving dikes that roughly parallel the margin, and dip steeply into the pipe. These resemble the sole faults or slip planes commonly present beneath landslides.

Fine Breccia.—Fine breccia occupies much of the inner part of the pipe and, where coarse breccia is absent, extends to the edge. Its intrusive relationships, small grain size, rounding of some fragments, heterogeneity of rock type, and siliceous dense matrix distinguish it from the coarse breccia.

Fine breccia intrudes the coarse breccia on a scale ranging from through-going dikes isolating large blocks of coarse breccia to branching and irregular veinlets filling fractures in coarse breccia blocks. Many dikes approximately parallel the edge of the pipe and intervene between the wall rock and masses of coarse breccia, suggesting that the fine breccia has wedged the coarse away from the adjacent wall. Where dikes cut coarse breccia composed of relatively small fragments, the edges of the dike are irregular and the dike incorporates some of the coarse breccia fragments. Dikes that cut large blocks have sharp contacts with local short apophyses. No dikes of fine breccia extend into the wall rock (Fig. 4).

In outcrop and hand specimen, the fine breccia consists of angular to round rock fragments in a dense siliceous matrix (Fig. 5). Quartz grains, feldspar crystals, and a few biotite flakes are present in minor amounts. The fine breccia is structurally homogenous. Flowbanding, lineation, foliation, shear or fault zones are lacking. Jointing is common but shows no pattern consistent enough to justify mapping.

Fragments range in size from microscopic to about 3 cm with a scattering of larger sizes. Most of them lie in the 5 mm to 2 cm range. Near the edges of the pipe, the fine breccia contains inclusions of coarse breccia; but

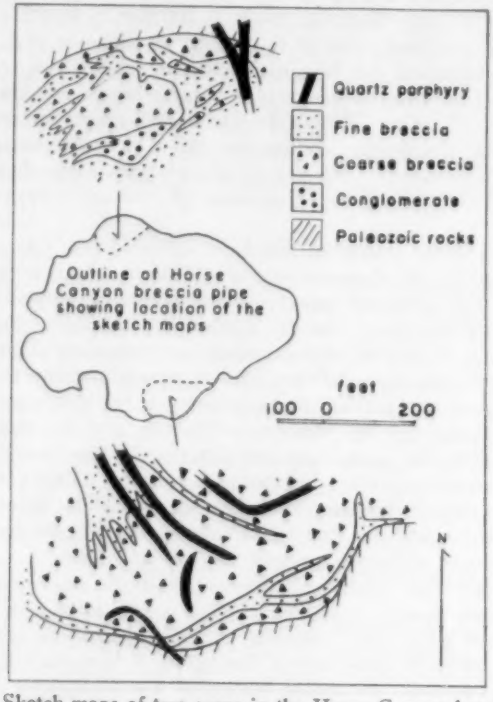


FIG. 4. Sketch maps of two areas in the Horse Canyon breccia pipe.

the bulk of it in the central part of the pipe consistently has a small grain size. In some of the narrow dikes and thin veinlets of intrusive breccia, grain size is smaller than elsewhere suggesting that perhaps the fragments of larger size were strained out during intrusion.

Most fragments are angular to subangular, but many, particularly of greenstone, shale and quartz, are subround to round. Many of the larger fragments, including quartz and feldspar grains, are fractured with slight displacement along the fractures but without complete disintegration.

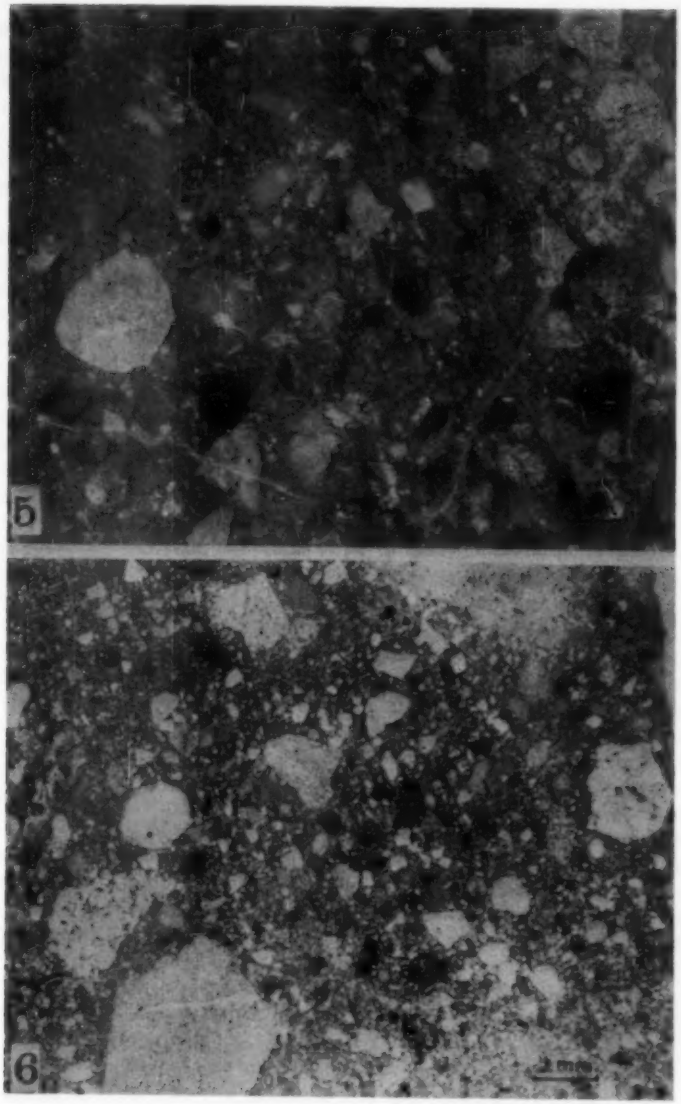


FIG. 5. Photograph of a slab of fine breccia, Horse Canyon pipe.
FIG. 6. Photomicrograph of the matrix of fine breccia, Horse Canyon breccia pipe. Plain light.

About one-half to two-thirds of the fragments are of Paleozoic chert, shale, quartzite, siltstone, and greenstone. The remainder are quartz monzonite, quartz latite and rhyolite porphyries, and quartz, plagioclase, biotite, and hornblende crystals, most of them fragmentary. Near the margins of the pipe and in dikes cutting the coarse breccia there is an increase in the proportion of fragments of the adjacent wall rock or coarse breccia, but even veins of fine breccia only one or two inches wide contain fragments of Tertiary porphyry and of Paleozoic sedimentary rocks, foreign to the adjacent rocks. The fine breccia has been thoroughly homogenized.

A careful search of more than 20 thin-sections in transmitted, oblique, and reflected light failed to find shards and pumice fragments. Many samples are devitrified and hydrothermally altered. Presumably, this alteration might have destroyed all evidence of shards; but, in other local rocks equally altered, some traces of shards can be seen. It is thus doubtful if shards were ever present in the fine breccia.

The fine breccia is a hard, thoroughly cemented rock. In hand specimen, the matrix appears glassy or porcelanous. All of the fine breccia is hydrothermally altered to some degree, most intensely near the central plug of quartz monzonite porphyry. Under the microscope, the few least altered samples have a matrix of dark brown glass crowded with small fragments of rock, quartz, and feldspar with minute specks and shreds of chlorite, sericite and clay, and with opaque dust. In most of the samples, the matrix is a patchy mosaic of quartz, chalcedony, feldspar, chlorite and clay; chert fragments are devitrified and recrystallized; feldspars are saussuritized; hornblende and biotite altered to chlorite and epidote; and calcite patches are scattered throughout the devitrified matrix, feldspars, and ferromagnesian minerals. Where alteration has been most intense, the chlorite of greenstone fragments has been altered to amphibole, and diopside has replaced the edges of some of the few limestone chips. Near the plug of quartz monzonite porphyry, there are many veinlets of quartz, a little potash feldspar, and few crystals of green hornblende. Pyrite and pyrrhotite are distributed throughout the fine breccia, and, in many places, a yellowish, birefringent, platey mineral, perhaps nontronite, fills spaces between fragments.

The matrix of the fine breccia thus is primarily a fine flour made up of rock and mineral fragments, and the cementation can be attributed to hydrothermal alteration and silicification, stemming in large part from the central quartz monzonite plug. The late quartz latite and rhyolite porphyry dikes also may have added to the hydrothermal alteration, as many of these have devitrified groundmasses and somewhat altered phenocrysts.

The distinctive characteristics of the fine breccia are its small grain size, its thorough mixing of fragments of Paleozoic sediments and Tertiary porphyry, its wide range in angularity, its high degree of alteration and devitrification, and its intrusive relationship to the coarse breccia and to the overlying conglomerate. The fine breccia clearly has had a history involving abrasion and brecciation of both wall rocks and intrusive Tertiary porphyries, thorough homogenization, and intrusion. Theories of its origin are deferred until other rocks in this and the other two pipes have been described.

Conglomerate.—Two blocks of Tertiary conglomerate are exposed on the north nose, one close to the marginal coarse breccia at an altitude of about 7,700 feet, and the other at an altitude of about 7,500 feet. Conglomerate also covers the east nose from an altitude of 7,000 feet, low in the pipe, to about 8,100 feet.

The conglomerate contains sand grains, pebbles, and a few cobbles of Paleozoic sediments and Tertiary prophyries and resembles the fine breccia in grain size and mixture of rock types. A greater proportion of rounded rock fragments and the presence of bedding distinguish the conglomerate from the fine breccia.

The bedding in the blocks on the north nose consists of lenses and streaks of subangular to round pebbles 2–3 cm in diameter interlayered with beds of sand size and of typical fine breccia. Cross-bedding and scour between beds is evident in some of the round pebble beds. In many places within the blocks, more or less vertical zones of fine breccia truncate the bedding. In other places, the bedding fades into typical unsorted fine breccia. Dips and strikes vary considerably within the block.

The conglomerate on the east nose is made up of small areas of lenses of bedded pebble conglomerate and sandstone mixed with much larger areas of unbedded, unsorted conglomerate that resembles the fine breccia except for the presence of many subround to round pebbles and a few cobbles. Individual beds or a sequence of several beds ranging in thickness from a few inches to 3 or 4 feet can be traced for as much as 50 feet and then grade into unsorted conglomerate or more angular typical fine breccia. A prevalent type of sorting consists of irregular, somewhat elliptical, pods of sand grains enclosed by coarse conglomerate. The reverse relationship is also present.

The presence of conglomerate as much as 1,000 feet below the upper limits of the pipe and from 200 to 1,200 feet below the neighboring spurs indicates subsidence. The subsidence need not have been as much as 1,000 feet as other evidence indicates that the volcanics in this part of the range buried considerable topographic relief.

The two blocks on the north nose are intruded and surrounded by fine breccia. Contact between fine breccia and conglomerate is well exposed on the west side of the north nose at an altitude of about 7,700 feet. The contact zone contains round pebbles and cobbles from the conglomerate enveloped in a matrix of fine breccia. Irregular tongues of fine breccia infiltrate the conglomerate, isolating individual pebbles or groups of pebbles. Here the fine breccia apparently intruded and mixed with poorly consolidated conglomerate. Another contact of the lower block of conglomerate with fine breccia, however, is sharp, the fine breccia truncating bedding in the conglomerate along a jagged irregular contact. Here the conglomerate was apparently well cemented.

The conglomerate apparently resulted from reworking of the fine breccia by running water. Much of it was a loose gravel, although locally some was fairly well cemented. The underlying fine breccia then apparently was mobilized; it intruded and mixed with the conglomerate, destroying much of

the bedding and leaving patches of bedding and confused masses of sorted sediments in a matrix of unsorted conglomerate and fine breccia.

Quartz Monzonite Porphyry.—The small plug of quartz monzonite porphyry covers an area of about ¼ square mile, in the bottom of Horse Canyon. The porphyry intrudes both fine breccia and conglomerate. An excellent exposure of the contact between porphyry and fine breccia is at an altitude of about 7,000 feet approximately 100 yards along the southeast fork of Horse Creek from its junction with the north fork. A pencil line could trace the contact for a distance of several hundred feet. The contact is highly irregular with apophyses of porphyry in the breccia and inclusions of breccia in the porphyry. The microscope shows that the porphyry along the contact contains many fragments of itself as well as the fine breccia, has a fine-grained granular groundmass, and is hydrothermally altered. Throughout the central plug are scattered inclusions of fine breccia, but they are most abundant along the margins.

The quartz monzonite porphyry worked its way towards the surface by intrusion and incorporation of the fine breccia that overlay it. The numerous porphyry fragments in the breccia and in the porphyry itself suggest that the rise of the magma was accompanied by several episodes of intrusion, chilling around its margins and in its offshoots, and brecciation. The subsidence of the conglomerate and the slumping of the walls of the pipe indicated by the coarse breccia may reflect episodes of subsidence of the magma. Furthermore, the alteration, both within the magma and in the surrounding fine breccia, indicates that the magma was evolving volatiles during its ascent. Intermittent rise of the magma and upward streaming of volatiles were probably the mobilization and intrusive forces behind the fine breccia.

Quartz Latite and Rhyolite Porphyry Dikes.—These dikes cut all other rock types within the breccia pipe except for hornblende andesite dikes. They also cross the margins of the pipe into the surrounding sediments. In mapping, it was not always possible to distinguish a rhyolite from a quartz latite dike in which hydrothermal alteration had destroyed the biotite. Hence the dikes are simply designated quartz porphyry on the map.

The dikes are discontinuous, range in width from 10 to 100 feet, trend northward, and are vertical or dip steeply to the west. This orientation of the dikes is common in this part of the range and is not controlled by structure peculiar to the pipe.

Near and parallel to their edges these dikes show excellent flow-banding in a dense, glassy, chilled marginal zone ranging in thickness from 1 to 16 inches. This chill zone has deep vertical grooves, resembling fault grooves or mullion structure, not only on the contact surface between porphyry and breccia, but also within the chill zone. They apparently were formed during intrusion.

Unlike the central plug, the dikes contain few fragments of breccia or conglomerate, and inclusions are very scarce throughout.

The flowbanding, mullion structure, and absence of inclusions of breccia suggest that these late dikes were much more viscous than the plug of quartz

monzonite porphyry. This high viscosity may have been due to a low content of volatiles, owing to their loss earlier during the eruptive activity.

Hornblende Andesite Dikes.—The final igneous event in the history of the Horse Canyon breccia pipe was the intrusion of a few, thin, discontinuous dikes of hornblende andesite. These cut the quartz latite dikes and occur both within and outside the pipe; they are sparsely but widely scattered over much of the range and presumably are not genetically associated with the pipes, at least in any direct way.

PIPE CANYON BRECCIA PIPE

General Description.—This breccia pipe is at the head of Pipe Canyon close to the Horse Canyon pipe from which it is separated by a narrow band of quartzite, chert, and greenstone. To the northeast it joins the Rocky Canyon pipe.

It has an irregular somewhat elliptical shape and a long diameter, oriented approximately northeast, of about ¾ mile. The west side is steep, but the east side appears to dip west, giving it an east-west cross-sectional shape like a tilted funnel. It cuts across Ordovician sediments and the thrust faults.

Units mapped within it include most of those of the Horse Canyon pipe, although some differ slightly in lithology: (1) coarse breccia; (2) fine breccia; (3) a plug and dikes of rhyolite; (4) dikes of pumiceous vitrophyre.

Coarse Breccia.—Patches of coarse breccia occur around the margins of the pipe but are less prevalent than in the Horse Canyon pipe. The largest exposure is along the south edge where Ordovician chert and greenstone have been broken into large blocks, tilted and rotated but not moved far from their original stratigraphic positions. The other outcrops are in the low saddle east of Peak "8101" and on the south slope of the south fork of Rocky Creek between the 7,400 and 7,600 foot contours.

In these two localities, the coarse breccia consists of fragments of chert, greenstone, siliceous shale, argillite, limestone, fine breccia, rhyolite, quartz latite porphyry, and pumice. Many fragments are subround and range in diameter from 3 inches to 2 feet. The matrix is composed of angular fragments of the same rocks and of quartz and feldspar, surrounded by finely comminuted rock flour filled with shreds and patches of chlorite and feldspar. This breccia has been thoroughly mixed, and the subround fragments indicate considerable abrasion.

Fine Breccia.—Fine breccia fills the southern and eastern half of the pipe. It intrudes the coarse breccia and, in turn, is cut by pumiceous vitrophyre, rhyolite, and quartz latite.

In grain size, shape and angularity of fragments, mixture of rock types, and absence of structure, this fine breccia resembles that of Horse Canyon. There is, however, a major difference: it contains many fragments of collapsed pumice, tuff, pisolitic tuff, and perlitic glass as well as the fragments of wall rocks and Tertiary prophyries. These volcanic rock fragments resemble the pyroclastics in foundered blocks in the Rocky Canyon pipe to the north. Alteration and silicification parallels that of the Horse Canyon pipe.

Pumiceous Vitrophyre.—Several dikes of pumiceous vitrophyre cut the fine breccia. These are off-shoots of the large mass that fills much of the Rocky Canyon vent, described later. Contact between the vitrophyre and fine breccia is sharp and excellent flowbanding parallels the contact. Where the dikes pinch out, the vitrophyre is crowded with inclusions of fine breccia.

Rhyolite Plug and Dikes.—A small plug of rhyolite occupies the west side of the pipe. It intrudes Ordovician rocks on the west and fine and coarse breccia on the south and east. Flowbanding is very faint or absent and inclusions of wall rock are sparsely scattered throughout.

A swarm of rhyolite dikes cuts the plug and radiates from it. The intrusive relations are very complex, and no attempt was made to map individual dikes. The dikes have flowbanded margins, columnar jointing normal to their contacts, and carry no wall rock inclusions. They cut not only the rhyolite plug, but also each other, the fine breccia, coarse breccia, and pumiceous vitrophyre. They represent a renewed influx of magma into the plug area.

ROCKY CANYON PIPE

General Description.—This pipe lies at the head of Rocky Canyon and extends along the ridge between Rocky and Lewis Canyons. It joins the Pipe Canyon pipe to the south. Rocky Canyon provides about 1,000 feet of relief in the pipe.

This pipe has a very irregular, almost triangular shape, about one square mile in area. An off-shoot extends to the northwest and another to the southeast to the west wall of Lewis Canyon. The east side of the pipe dips steeply west to northwest. The west and north side are almost vertical.

The units mapped are: (1) coarse marginal breccia; (2) tuff, tuffaceous sediments, and dacite block agglomerate; (3) pumiceous rhyolitic vitrophyre; (4) rhyolite and quartz monzonite porphyry dikes.

Coarse Breccia.—The east edge of the pipe is well exposed and is free of coarse breccia except around part of the small off-shoot on the west wall of Lewis Canyon. Here vitrophyre intrudes a coarse breccia composed of large and small blocks of Paleozoic chert, greenstone, and quartzite, and of Triassic grit and limestone conglomerate. The immediately adjacent wall rocks are chert, and the nearest quartzite, greenstone, and Triassic rocks are on higher thrust plates above the breccia outcrop. Alluvium and landslides cover the west and north margins.

Tuffaceous Sediments.—Several large blocks of bedded tuffaceous sediments, dacite agglomerate, and conglomerate have foundered in the Rocky Canyon pipe and are now tilted at various angles and surrounded by pumiceous vitrophyre as much as 300 feet below neighboring ridges and peaks. Bedding in the largest block dips 30 to 55 degrees east and, in the smaller blocks, from 60 to 90 degrees in various directions. Within the blocks are many folds and faults too small to show on the map.

These sediments include: stream-deposited rock fragments and ash in beds that show cross-bedding, cut-and-fill structures, and scour along bedding planes; massive or crudely-graded beds of shards and pumice, probably air-

laid ash falls; massive layers of tuff-breccia; and lenses of probable pond or lake deposits of very fine ash having thin laminations and cross-bedding.

Tuffaceous layers of shards and rock fragments of sand size carry spherical pellets about 5 mm in diameter. Around a center of coarse fragments is a concentric shell in which the grain size decreases outward and shards and rock fragments are so oriented as to give a concentric foliation. Some of the pellets or pisolites are slightly flattened parallel to bedding and others are broken.

Perret (15) has described similar pellets formed by accretion of ash in a moisture-laden eruption cloud. Tanakadate (20, p. 165) found pellets formed by the snow-balling of ash, wet from rains and melting snow, down volcanic slopes in Japan. Rust (19, p. 65–69) attributed concentric pisolites in breccia pipes in Missouri to accretion in an atmosphere of magmatic spray during explosive eruptions.

Grain size in the bedded tuffaceous sediments ranges from the limit of the resolving power of the microscope to fragments of pebble size. Most of the beds are composed of sand, grit, and pebbles, ash and lapilli. Transport by streams was relatively short, as angular to subangular fragments predominate over rounded ones. About 30 percent of the sand grains, pebbles, and cobbles are of Paleozoic sedimentary rocks, and greenstone and the remainder are Tertiary porphyries, glass shards, pumice lapilli, perlitic glass, quartz and feldspar crystals.

Within the blocks of tuffaceous rocks are lenses of hornblende dacite agglomerate. Roughly spherical blocks of dacite porphyry ranging from 1 to 6 feet in diameter lie in a matrix of fractured crystals of quartz, hornblende, and plagioclase and angular fragments of dacite. The dacite is much altered and oxidized.

Explosive volcanism preceded eruption of the pumiceous vitrophyre. The coarse grain size, angularity of fragments and presence of pisolites and block agglomerate suggests a nearby source of the eruptions. The lake beds might have formed in small lakes occupying a caldera in the pipe.

The fragments of Paleozoic sedimentary rocks in the bedded rocks of the foundered blocks have the same general size range, the same general proportions of different lithologies, and the same degree of rounding as the fragments of the Paleozoic rocks in the fine breccia of the Pipe Canyon pipe. Fragments of tuff, perlitic glass, and pumice like those in the tuffaceous sediments are abundant in the fine breccia. This suggests several cycles of brecciation, explosive volcanism, and reworking and deposition by running water. Unfortunately, the absence of contacts between the fine breccia of the Pipe Canyon pipe and the tuffaceous sediments of the Rocky Canyon pipe precludes any firm conclusions regarding their mutual relations.

Pumiceous Vitrophyre.—The main body of vitrophyre occurs between the north and south forks of Rocky Creek. Several dikes extend into the fine breccia of Pipe Canyon, and a small off-shoot intrudes chert on the west wall of Lewis Canyon. Except for this off-shoot, dikes of vitrophyre do not intrude the wall rocks of the vent.

The vitrophyre is clearly eruptive from below. Flowbanding and lineation formed by stretched vesicles and pumice fragments generally dip steeply to the west and northwest, but marked deviations here and there suggest considerable turbulence.

Contacts of the vitrophyre with the blocks of tuffaceous sediment are gradational through a zone ranging from 25 to 200 feet in width. A traverse across one contact zone showed the following sequence: (1) banded and lineated pumiceous vitrophyre containing scattered inclusions of Paleozoic rocks and Tertiary lavas and tuffs; (2) banding and lineation gradually fade and the number of inclusions increases; (3) structure disappears altogether and inclusions, some angular and some rounded, constitute most of the rock, which now resembles a tuff-breccia; (4) faint and distorted patches and lenses of crude sorting and bedding appear and gradually increase in distinctness until the rock is a well-bedded water-laid tuff and tuffaceous conglomerate.

The fact that the blocks of tuffaceous sediments are steeply tilted and deformed and completely surrounded by vitrophyre rules out the possibility that this gradational contact portrays reworking of the vitrophyre after emplacement. The vitrophyre appears to have engulfed comparatively unconsolidated tuff and tuffaceous sediments, stirred and destroyed the bedding, and incorporated fragments from them.

Throughout the main mass of the vitrophyre are numerous chips and fragments of Paleozoic sedimentary rocks, Tertiary porphyries, and glassy, tuffaceous, or pumiceous volcanic rocks. In addition, thin pods or lenses of breccia, consisting of a mixture of coarse and fine, angular to subround, fragments of many rock types, resemble the coarse breccia of Pipe Canyon. Also, within the well lineated and banded vitrophyre are ill-defined areas with gradational boundaries, which lack vesicles and vugs and consist primarily of rock fragments resembling these of the fine breccia of Pipe Canyon. Probably the Rocky Canyon vent was once largely filled with breccia like the Pipe Canyon breccia pipe and some of this breccia was incorporated in the pumiceous vitrophyre.

In outcrop, the pumiceous vitrophyre is light gray to white and has a porcelanous surface texture. Abundant strung-out lenses of inclusions, the approximate alignment of flat chert chips, the open lense-shaped vugs on weathered surfaces, and stretched out vesicles and fragments of collapsed pumice show flowage. The flow structures wrap around the large inclusions and show many swirls and intricate folds.

Thin sections show that the vitrophyre is a rhyolite consisting primarily of vesicular glassy lava and pumice fragments forming a matrix enclosing inclusions of rock, and quartz, plagioclase, and sanidine crystals (Fig. 7).

Its most striking characteristic is its vesicularity. Most of the rock is crowded with small vesicles stretched so that their cross-sectional width is but a fraction of their length. In some slides, vesicular lava can be traced unbroken across the length of the slide. In others, the rock is made up of many stretching and flattened fragments of pumice.

In addition to the small vesicles, large elliptical vugs as much as 3 mm in length and 1 mm thick are common. Many of these vugs contain an inclusion at one end, and, in any particular slide, all such inclusions are at the same end of the vugs. The small vesicles flow around the large vugs as well as the inclusions. Apparently many of the vugs formed because turbulence around the inclusion localized evolution of gas from the magma.

In many slides, inclusions of chert or porphyries have been fractured; the individual fragments have been slightly rotated and pulled apart; and vitrophyre has flowed into the gap but only partially filled it, leaving a dumbbell shaped vug with an inclusion of the same rock type at each end. This suggests that a viscous magma evolved gas into areas of slightly lower pressure formed by the fracturing and pulling apart of the fragments.

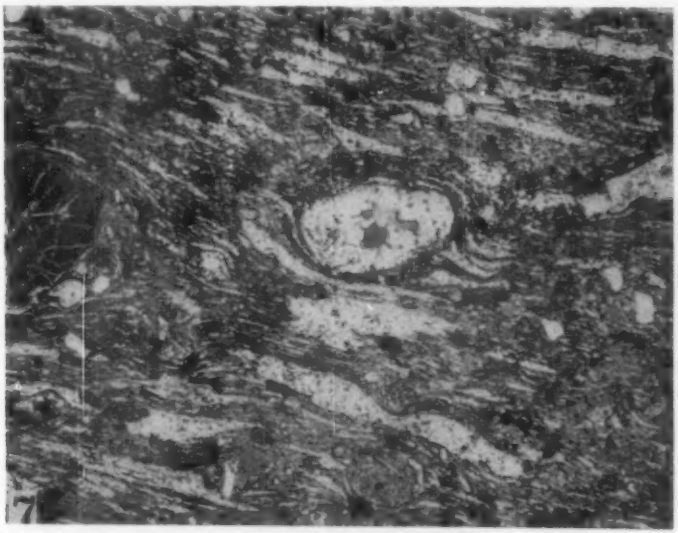


FIG. 7. Photomicrograph of pumiceous vitrophyre, Rocky Canyon pipe. Crossed nicols.

Alteration and devitrification of the pumiceous vitrophyre are widespread. Feldspars are saussuritized; hornblende and biotite in inclusions are converted to chlorite, magnetite, calcite, and quartz. The glassy vesicular groundmass is devitrified and filled with wisps and irregular patches of a yellowish brown birefringent mineral, probably an iron-bearing montmorillonite. Vesicles and vugs are filled with opal, chalcedony, quartz, and the brown clay mineral.

The devitrification was patchy. In some devitrified rocks, the original pumiceous texture is clear. In others, under plain light, devitrification appears to have almost destroyed the pumiceous texture, and reflected or polar-

ized light is required to see it. Many intensely devitrified patches are along minute cracks, some of which slightly offset the vesicles. This suggests two generations of devitrification, the first resulting from gases within the magma and vesicles, and the second from vapors ascending cracks after consolidation.

The pumiceous vitrophyre erupted as a viscous magma. In some places it remained liquid enough to flow without fracturing, elsewhere it became so viscous, probably from loss of volatiles to the vesicles, that it became fractured. The numerous vesicles and vugs and the widespread devitrification and alteration show that it was evolving much gas, indicating a rapid decrease in confining pressure, which in turn suggests rapid ascent. On reaching the surface, it may well have poured out as a greatly expanding mass of shards and pumice in a cloud of its own gases to form a welded tuff.

Rhyolite and Quartz Monzonite Dikes.—Along the east edge of the vent is a discontinuous dike of altered quartz monzonite porphyry that separates vitrophyre from Ordovician rocks. The final event in the formation of the vent was the intrusion of dikes and small pods of rhyolite, particularly along the edges of the northwestern off-shoot. The rhyolite carries no inclusions and has excellent flow-banding.

SUMMARY

Although the three breccia pipes differ in details of lithology and distribution of rock types, they are generally similar. The pipes were conduits for rising plugs of volatile-rich magma ranging from quartz monzonite to rhyolite. This magma worked upwards by repeated intrusion and incorporation of a fine breccia that apparently filled most of the pipes above the magma. This fine breccia in turn intruded coarse breccia, formed by slumping of the walls of the pipes during episodes of subsidence, and conglomerates (in the Horse Canyon pipe) produced by reworking of the breccia by surface waters. The rise of the magma was accompanied by explosive eruptions in the Rocky Canyon pipe and perhaps in the Pipe Canyon pipe. Intrusion of viscous dikes presumably low in volatiles due to their loss in earlier eruptions brought the volcanic activity to a close.

ORIGIN OF BRECCIA PIPES

Many breccia pipes and vents filled with fragments of bed-rock have been studied and several theories of origin proposed. The following are representative samples culled from a review of the literature.

Thompson (21) concluded that solution stoping formed the breccia pipes of carbonate rocks in the Terlingua quicksilver district of Texas. He wrote (p. 35):

> The fact that the breccia is displayed vertically downward in all pipes indicates that they formed as a result of solution in the Devils River limestone and collapse-stoping of overlying strata. The dissolving agent is believed to have been hydrothermal solutions, but meteoric water is a possible alternative.

Locke (10) has proposed essentially the same idea for the origin of the Pilares breccia pipe of Sonora, Mexico, a pipe composed of mineralized, altered, and subsided andesite fragments.

In the Shoshone Range, the dominantly siliceous sedimentary rock fragments show no evidence of widespread solution; solution stoping does not appear to be applicable.

Burbank (6, p. 170–171) described breccia pipes in the Red Mountain mining district of Colorado which have several features resembling those of the Shoshone Range pipes:

> The pipes are nearly vertical cylindrical bodies of slightly elliptical cross-section, occupied by breccias and by intrusive bodies of quartz latite porphyry and rhyolite . . . In the more complex pipes the age relations show that breccia was formed first and was followed by intrusions of quartz latite and finally rhyolite.

Many of the pipes are surrounded by a well defined outside wall of vertical sheeting and a zone of curving or spiral fractures in the surrounding wall rock. In many pipes, the breccia grades into the country rock. Burbank (6, p. 177–178) pictured their formation thus.

> The passage of magmatic emanations up through favorably jointed and fissured rock may have caused certain chemical or volume changes along some vertical zone of greatest concentration, which impaired the strength of the rock and induced local crackling and crumbling. The zone of disintegration spread outward from the axis along generally curving surfaces—first as the spiral form, controlled by yielding of the rock along planes of maximum shearing stress, and later as the concentric form, controlled by the increasing stresses surrounding the plastic core. As the breccia mass spread into the surrounding rock it tended to assume the form either of a ring zone, or of a cylindrical core.

This hypothesis is difficult to apply to the Shoshone Range because the vertical sheeting and curving fractures are lacking, the contacts of the breccia with wall rocks are relatively sharp, and the pipes and vents are flaring.

The classic areas of Tertiary volcanism in the British Isles provide many examples of breccia believed formed primarily by violent explosive eruptions, many of which are clearly associated with rising acidic magmas and are located along ring dikes (23; 2, p. 199–210; 18, p. 806–810; 17). Tyrrell (23, p. 182) described this example from Arran:

> The explosion-breccia of the Central Ring complex consists of a heterogeneous accumulation of fragments of all sizes, ranging from masses hundreds of yards across, down to microscopic chips. The large masses are much fissured, broken, and tumbled; and many of the smaller fragments have suffered micro-brecciation which can be seen even in a microscopic section. The fragments are composed of Old Red Sandstone and Mesozoic rocks which originally spread over the explosive foci, and had already been domed and fissured as the result of the earliest igneous activity of the episode; fragments of the basaltic lavas which were erupted at the earliest stage; and fragments of the acid igneous rocks whose intrusion and explosive condition were the prime causes of the general fragmentation.

A large crater-forming explosion or a sequence of them accompanied by infilling of the crater by debris hurled into the air and by slumping from the walls is not adequate to explain the complexity of the Shoshone Range breccia

pipes—the intrusive relations of the fine breccia, the heterogeneity of rock type and homogeneity of grain size of the fine breccia, the absence of shards and tuff in the fine breccia of Horse Canyon, and the episodes of subsidence followed by remobilization of the fine breccia. This does not rule out, however, crater-forming explosions as contributors to the brecciation.

Several theories attribute the origin of breccia pipes and intrusive breccias to repeated or intermittent gas fluxing and explosive activity, not necessarily beginning with a single gigantic explosion. The growth of the breccia and its containing pipe or vent is gradual. Attrition by fragments in the gas stream as well as the explosive power of the gases themselves is an important agent of further brecciation and of erosion of the walls.

H. Cloos (7) concluded from his detailed study of the Swabian pipes that gas from an underlying magma seeks the surface through fissures and cracks. When it breaks through, confining pressure is greatly reduced, and the gas streams upwards. With the aid of fragments torn from the wall rocks and lapilli from the magma below, the gas gradually widens the vent by attrition, abrasion, and the quarrying action produced by injection into cracks. The Swabian pipes have many of the features of the Horse Canyon pipe, including large blocks of wall rock only slightly depressed from their original positions and surrounded and intruded by fine breccia, which in the Swabian pipes contains much lapilli.

Williams (25, p. 179) has postulated a somewhat similar mechanism for formation of the breccia-filled vent at Marysville Buttes:

> The first steam eruptions may have issued from a narrow fissure that widened in depth. Such a fissure may have been enlarged partly by the actual violence of the later explosions and partly by the heating and fracturing of the wall rocks. Detached blocks falling into the vent between successive eruptions and hurled upwards by steam under high pressure would provide powerful tools for the widening of the crater. In a similar manner, ejecta falling back into the crater during an eruption and being repeatedly thrown out would aid materially in widening the aperture.

The Cripple Creek, Colorado volcanic center has been carefully studied by Lindgren and Ransome (9), and Loughlin and Koschmann (11). It is a complex of breccias, lavas and intrusive rocks in which sedimentary rocks have been buried to great depths. It was formed by repeated eruptions, intrusions, and brecciations and the coalescing of a number of vents, pipes, and craters. Cross-sections of the Cripple Creek crater (12, pl. 29) are remarkably similar to that of the Pipe Canyon-Rocky Canyon pipe complex.

Many of these breccia pipes and vents have puzzling features that raise questions as to the exact mechanism of the gas-impelled brecciation. Lovering and Goddard (12, p. 297) write of the Cripple Creek volcanic center:

> The action itself was complex, and some of its effects are difficult to understand, for example, the reduction of volcanic rock or granite to fine debris without appreciably disturbing the position or alignment of large blocks that escaped comminution. Fine debris was forced between blocks of granite which today are found essentially in their original positions but widely separated from the nearest granite wall of the crater.

Richey (17, p. 168) noted that the walls of many of the vents in Mull and Ardnamurchan are shattered with little displacement of the wall rock fragments and that, in some of the volcanic districts, brecciated rock at depth remained in place. Rust (19, p. 60) found that breccia pipes in Missouri show definite concentrations of fragments of one particular wall rock type. Anderson, Sholtz, and Strobell (1, p. 40) have described breccia pipes from the Bagdad area, Arizona, in which stratigraphy of the wall rocks can be traced through the breccia in the pipes without appreciable displacement.

Rust (19, p. 71–72) called breccia formed in place "authigenic explosion breccias" and proposed the following explanation which was also accepted by Richey (17, p. 168):

> Surrounding the confined gas column would be an aureole of rock under the same gas pressure as that in the tube. The amount of gas in this rock would depend on its porosity. At the culmination of the explosion, the compression on the walls and that of the gas contained in the pores of the walls would be at a maximum. . . . Following the explosion, the pressure in the tube would quickly drop to the atmospheric pressure or even less. Slightly after the explosion in the tube there would then be a counterexplosion of the confined gas in the pores of the wall rock, directed toward the center of the tube. This would cause shattering of the gas-bearing rock and projection of great quantities of it into the tube. . . .

"Fluidization"—an industrial process in which gas flowing through a bed of fragments causes violent agitation of the fragments and expansion of the bed until the mass has all the characteristics of a mobile fluid—has been applied by Reynolds (16) to comminution of bed rock to fragments, intrusion of breccia, and authigenic explosion breccias. She cites many examples of this process including the Swabian pipes and many of the Tertiary vents and breccias of the British Isles.

Tweto (22, p. 527) noted that many of the Pando sills in Colorado were preceded by lenses of breccia containing fragments of the sill and of the surrounding sediments. He concluded that gas, expelled by chilling of the magma, brecciated the rocks in advance of the intruding sills and aided in their emplacement. Such a process might also assist in the rise of dikes of magma through overlying rocks.

In addition to these possible mechanisms for brecciation of country rock in volcanic areas, there is another one which was briefly mentioned by Locke (10, p. 446) but which perhaps deserves more consideration than has been granted it heretofore. Rock-bursting occurs both in quarries and in mines and can cause brecciation on a large scale.

White (24, p. 3–6) described rock-bursting in granite quarries at Barre, Vermont as follows:

> . . . cracks that formed during or following quarrying operations . . . slope in all directions and may be gentle or steep. It is clear, therefore, that they have no consistent relationship to natural parting surfaces, sheeting, planar structures, and boundaries of the granite, all of which have a more or less constant orientation throughout the district. . . . The cracks have a very consistent relationship to the shape of the quarry in which they lie; without exception they slope toward the deepest adjacent opening or free face. They are certainly the result of the tendency

of the granite to expand into the quarry opening . . . the force is tremendous and more than adequate to distort and break large blocks of granite.

Bain (3, p. 715) found that in some marble quarries the rock burst with such violence that channeling machines weighing many tons were thrown from their tracks. By careful measurement, Bain ascertained that the expansion was volumetric.

The Report of the Witwatersrand Rock Burst Committee (26, pp. 14–15) gives this graphic description of a rock-burst in one of the deep Rand gold mines:

. . . without any warning a sudden shock extinguished all lights in the area affected and the footwall appears to rise and the hanging wall to descend. Props are shattered, pigstyes and packs are compressed, and quantities of rock burst from the faces of the stopes, from pillars, from dykes or other remnants of ground which have been left unworked, and from the sides and roofs of levels. Tracks are buckled and displaced and pipelines bent or broken; cracks open along fault planes and sometimes the rock along the fault is so shattered and brecciated that quantities fall into mine excavations. Often, with the shock, the solid face of a stope or pillar punches into and shatters the hanging wall or both of those walls in its vicinity and the falls from the hanging wall so caused may result in even more loss of life than the actual burst from the face. The shock may also shake down slabs of hanging wall at some distance from the place where the burst occurs. After a severe burst, it is frequently the case that movements immediately cease, but sometimes movement of the hanging wall will continue more or less spasmodically for some hours or even days.

Violent rock-bursts may be accompanied by an air blast which causes further breccia and the formation of fine dust. Crane (8, p. 35–36) thus describes an air blast in the Lake Superior copper mines:

The air being expelled violently from the workings through the shafts caused much damage underground and forced out of the mine great volumes of air charged with dust, dirt, and small fragments of rocks, sticks, and other debris, which rose 150 feet or more in dense columns, the larger pieces of rock, sticks, and clothing, and debris falling back at a height of 50 to 60 feet. The air was so filled with dirt and small particles of ore that they obstructed the view and cut the face and hands like a sandstorm. Furthermore, everything in the mine was covered with a thick layer of dust, so thick, in fact, that it was difficult to distinguish the bodies of men killed in the blast from rock and timber.

Rock-bursting in mines may take several forms. Large bodies of rock may be completely brecciated with relatively little movement of the body as a whole. Near Johannesburg a block of ground weighing an estimated 500,000,000 tons broke up in sections with a movement at the surface of only 2 or 3 inches and at the 14th level of about 9 inches (26, p. 13). Crane (8, p. 37) reported that rock-bursting on one of the Lake Superior mines produced cracks in the surface rocks from one-half to one mile away.

At the other extreme is the spalling or spitting of small flakes of rock from a face.

. . . he heard a report like that made by a saloon rifle. A native . . . was struck and cut by a flat irregularly shaped stone ¾ inches thick and 3 lbs. 3 oz. in weight

which flew from the face. Immediately afterwards a stone about 12 inches by 8 inches was seen gradually peeling off the face about 30 feet away . . . a lenticular stone about 7 inches in diameter and ¾ inches maximum thickness flew from the face to a distance of 12 feet with a report similar to that previously heard. (26, p. 8).

Between these two extremes are many variations in the type of rock-bursting and its products. Crane (8, p. 160) distinguished three types of less violent rock-bursting: (1) flaking or spitting, (2) spalling in which large fragments thin in comparison with their width break from the face, and (3) wedging, the breaking of large masses, often weighing tons, from pillars. The result of various forms of rock-bursting is to surround some tunnels and stopes with a zone of brecciated wall rocks and in some instances to arch or dome a stope upwards leaving a much larger area of broken rock than was originally mined.

Rock bursts can produce a variety of breccias. Some are incoherent masses of angular fragments of all sizes ranging from dust to blocks weighing tons. Others consist of small fragments described as "small as a man's fist," or "small stone like road-metal." One observer reported complete disintegration of a hanging wall "so that it had little more cohesion than sand" (26, p. 12, 14).

The depth at which rock-bursts begin to occur differs from place to place and from mine to mine. In the Rand gold mines, it becomes a serious problem at 2,000 to 3,000 feet (26, p. 38). In the Lake Superior copper mines, rock failure begins at about 1,000 feet and increases in intensity with depth. In almost any mine, it is a constant hazard at depths of 6,000 feet or greater (8, p. 38).

Rock-bursting is most violent in the flintiest, most silicified rocks. In the Rand, the massive quartzite of the hanging wall readily bursts (26, p. 21), and in the Lake Superior region the hard, strong, and brittle trap bursts most frequently. Crane (8, p. 6) concludes as a rule of thumb that rock which is hard to drill is the most explosive.

The immediate cause of rock-bursts is excavation of the rock, leaving free faces. Other conditions being favorable, the rock will burst if an opening is made in it. The rock is under stress, primarily from the weight of superincumbent rocks, although other factors have been cited (5, p. 30). When part of the stress is relieved asymmetrically by formation of a free face, the stress becomes directed towards the opening, the rock becomes strained and, if strained beyond its elastic limit, will brecciate and burst into the opening.

Bridgeman (4) subjected cylinders of crystals and of porphyry, andesite, and granite in which a cylindrical interior hole had been drilled to high hydrostatic pressure up to 7,000 kg/cm^2 and found that the cylinders failed by a mechanism resembling rock-bursting. The cavities were enlarged and filled with fragments of irregular shape and size that had flaked or spalled off the sides of the interior cylindrical hole. In the porphyry and andesite, there was no cracking or flowage of the remaining outside shell of rock, and, in the granite, slight flowage occurred without fracturing. Bridgeman (4, p. 266–267) summed up his results thus:

> Cavities in the materials dealt with in this paper, which may be broadly characterized by the property of brittleness, exhibit a method of failure under high compressive stresses not shown by ductile materials like metals. This method consists of shooting-off of minute fragments with considerable violence from the walls of the cavity. . . . The frequency, and probably the velocity, of projection becoming greater at higher pressures. This method of disintegration is shown by rocks and by single crystals; in rocks, the splinters show no relation to the boundaries between chemically homogeneous parts of the mixture, and, in crystals, there is no obvious connection with the crystalline symmetry.

In a volcanic area, especially where the rocks are brittle and siliceous as in the Shoshone Range, rock-bursting might occur if free faces were formed. Such faces might result from a drop in magma level in a chamber caused by intrusion or extrusion elsewhere, be formed along fractures made by movement or pressure of magma or gases, or be left as the walls of a pipe after a gas eruption. Furthermore, if gas under confining pressure broke through to the surface and rapidly gained velocity up a pipe, the pressures on the pipe wall would be greatly reduced as the pressure energy was converted to kinetic energy, much as in a Venturi tube. If other conditions were favorable, the rocks of the walls might burst into the gas stream and might even eventually choke it when the eruption began to diminish. Rock-bursting would be effective in widening gas vents and in forming large masses of breccia such as that filling the Horse Canyon pipe. However, it does not explain many other features, the intrusive relations of the fine breccia for instance, and to assign to it the entire role in formation of the breccia pipes and vents would be to ignore all the evidence of explosive eruptions.

ORIGIN OF THE SHOSHONE RANGE BRECCIA PIPES

Any picture of the formation of the breccia pipes must necessarily be complex and probably involves a combination of many of the foregoing mechanisms, the importance of any particular one being difficult to assess. Brecciation in the Shoshone Range preceded intrusion of magmas rich in volatiles; the breccias themselves show much hydrothermal alteration; and explosive tuff and agglomerate eruptions occurred. Evidently gases played an important part. Likewise various forms of rock-bursting and collapse stoping may have contributed to the brecciation.

Assume a rising cupola of magma which is crystallizing and building up pressure of volatiles and is perhaps preceded by a cap or aureole of gas (Fig. 8). The pressures of magma and gas open cracks overhead; gas rushes into some of these, tearing fragments from the walls which, in turn, assist in further brecciation by abrasion, attrition, and wedging; magma rushes into others, quickly chills and evolves more gas which brecciates the rocks ahead; still others may be filled with breccia formed by rock-bursts. Rapid heating of the rocks and conversion of included water to steam may add to the fragmentation. Thus a helmet of breccia forms ahead of the rising magma by a variety of processes, and this breccia, in turn, becomes intrusive itself.

If the gases or magma find access to the surface along cracks or fissures, an explosive eruption follows, which perhaps forms a small crater and also

causes further brecciation by the rapid escape of gas, perhaps by rock-bursting into the pipe, and perhaps by "authigenic" brecciation. Once the pressures have been diminished by eruption, a period of subsidence follows, accompanied by slumping, collapsing, and perhaps rock-bursting, which further enlarges the volume of breccia ahead of the main body of magma. The latter invades the breccia in dikes and apophyses and solidifies; fragments of the breccia are incorporated into the upper parts of the magma. As the magma continues to cool and crystallize, gas pressure builds up again. Another cycle of eruption, brecciation, and intrusion of magma and gas follows.

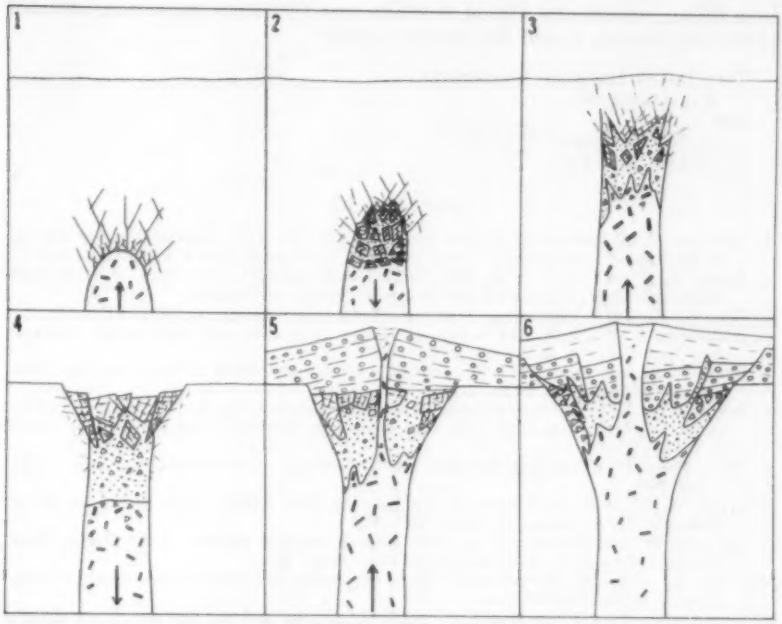


FIG. 8. Schematic diagram showing steps in the formation of the breccia pipes.

Dikes of magma previously injected into the breccia are fractured and their fragments added to the breccia. Each successive cycle of eruption, brecciation, and subsidence increases the volume of the breccia, grinds it to a finer grain size, rounds some of the fragments, and thoroughly mixes them. The magma becomes more and more filled with inclusions. Eventually the breccia works its way to the surface where it intrudes and mixes with breccias and tuffs formed by previous eruptions. There it is also reworked by streams and perhaps covered by tuffs and extrusive breccias. Subsidence occurs again; the walls of the now open crater tend to landslide or rock-burst; another intrusives impulse mobilizes the fine breccia which surrounds and injects the

coarse breccia and wedges large blocks away from the walls along landslide sole fractures. The intrusion need not be violent. The fine breccia, probably enveloped in steam or hot water of both juvenile and meteoric origin may have behaved essentially like a magma rising and falling in a conduit.

In the Rocky Canyon pipe, the magma perhaps broke through to the surface to form a welded tuff. Whether or not the quartz monzonite porphyry of the Horse Canyon breccia pipe also did so is not known; but the absence of lapilli and shards in the fine breccia suggests that an explosive eruption did not occur. The main magma bodies lost their volatiles, cooled and crystallized. Silicification, devitrification, and alteration cemented the breccias. Late dikes, viscous and low in volatiles, and free from inclusions, intruded cracks and fissures to end the volcanic activity.

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APPLICATION OF X-RAY SPECTROMETRIC ANALYSIS TO GEOCHEMICAL PROSPECTING

G. R. WEBBER

ABSTRACT

X-ray spectrometry can be applied to the determination of variation of metallic elements in soils and related materials. This method of analysis is rapid, relatively inexpensive, nondestructive of sample and permits the detection of many elements. The accuracy obtained depends largely on standards available and the method of sample preparation used.

Various methods of sample preparation can be used to suit the purpose of the analysis; for example, direct use of the powdered sample, acid extraction and analysis of the resulting solution, or analysis of an evaporated concentrate from the acid extraction. Examples of applications of these techniques to analysis for zinc, iron, manganese, copper, lead, and nickel are given.

INTRODUCTION

INTEREST in geochemical prospecting as a means of mineral exploration has resulted in the development of many rapid analytical tests. Many of these are field tests that can be carried out on the spot. Some of these tests are nonspecific and give a "total metal" value that represents the net effect of the presence of several metals. Many are specific for one or another metal. As part of an investigation into the application of x-ray spectrometry to geological materials, the application of the x-ray spectrometer to analysis of soils and related materials was tested in the Department of Geological Sciences at McGill University. Use of x-ray fluorescence for the analysis of soil samples has also been described by Adler and Axelrod (1) and Salmon (2).

GENERAL PRINCIPLES OF X-RAY SPECTROMETRY

The general principle of x-ray spectrometry is that a sample, which may be in solid, powder or liquid form, is bombarded with x-rays from an x-ray tube; secondary x-rays, having wavelengths characteristic of the elements in the sample, are emitted from the sample and these x-rays are dispersed by an analyzing crystal so that the different wave lengths can be distinguished. A geiger tube or other detecting unit is used to measure the rate of x-ray pulses. In general, an increase in the concentration of an element in the sample produces an increase in the pulse rate of x-rays of that element. For a more detailed account of the theory and equipment of x-ray spectrometry, see Cullity (3). The journal "Analytical Chemistry" contains review articles and many papers on applications of x-ray spectrometry.

Figure 1 shows a copy of an x-ray recording of an artificial sample containing a large number of elements. It must be emphasized that various

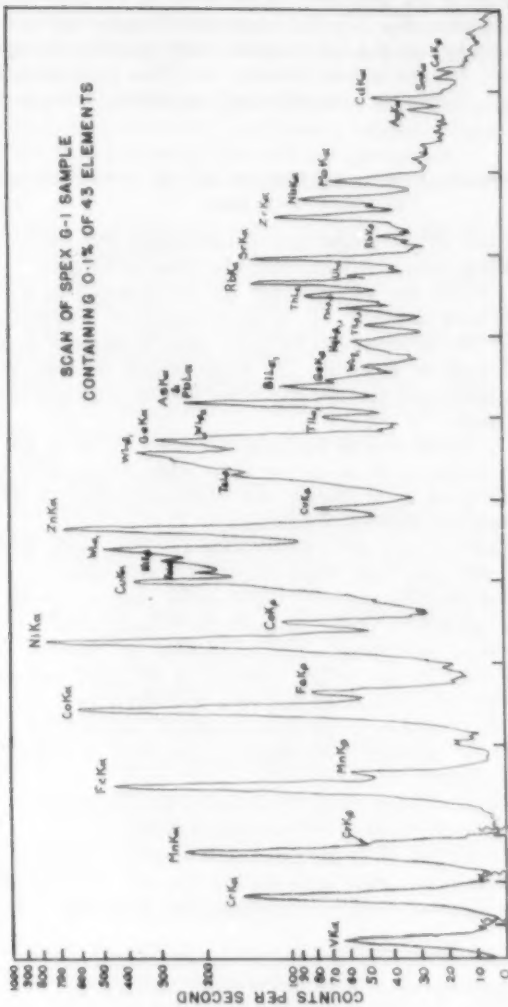


FIG. 1. Spex standard G-1, available from Spex Industries Inc., 80–56 230th Street, Queens Village 27, 27, N. Y., containing 0.1 percent of each of 43 elements.

combinations of instrumental components can be used to obtain maximum sensitivities in different regions of the x-ray spectrum. The counting tube used in the illustration is not very efficient for peaks of low wavelength such as molybdenum or niobium Kα. In the longer wavelength region, the sensitivity can be increased by use of a helium path which has less absorption than air for these x-rays. By this means intensity for TiKα radiation can be increased eight times. Notice the simplicity and regularity of the x-ray spectrum.

ADVANTAGES AND DISADVANTAGES OF THE USE OF AN X-RAY SPECTROMETER FOR SOIL ANALYSIS

There are a number of advantages and disadvantages that the x-ray spectrometer presents when compared with other analytical techniques.

Advantages: 1. The x-ray spectrometer can be operated at a relatively low cost after it has been acquired. 2. A large number of different elements can be detected. 3. The analysis can be made quite accurate if desired. 4. The spectrum is simple to interpret. 5. Analysis can be very rapid. 6. Analysis is nondestructive and permits easy recheck of an analytical determination on the same sample.

Disadvantages: 1. Initial cost of equipment is high. 2. It is not possible to do on-the-spot analyses such as can be done with colorimetric tests. 3. Sensitivity is not as good as is desired for many elements. 4. Electronic equipment is involved and requires maintenance.

Some of the disadvantages are not as great as they might seem. The initial cost is not really very high when considered with relation to the exploration budgets of mining companies. Colorimetric analyses can be done on the spot, but many companies prefer to have their samples collected in the field and analyzed at a base camp where conditions for analysis are more convenient. If the samples are to be collected in the field and sent to a laboratory, they could just as easily be sent to a base camp for x-ray analysis. The establishment of a permanent or semipermanent location for the x-ray spectrometer would be desirable. It might be possible to make the unit portable to a certain extent.

The detection limit of many elements on the x-ray spectrometer may be lowered by preliminary chemical enrichment procedures.

The problem of maintenance of the equipment is not as serious a difficulty as it would have been a few years ago, because the use of electronic equipment is much more general now, and improvements have been made in instrumental design.

COMPLICATIONS IN QUANTITATIVE ANALYSIS

Use of the x-ray spectrometer for quantitative analysis is complicated by variations in sample matrix that can affect intensities of the emitted x-ray peaks. Various methods are available to eliminate or minimize such effects. These involve such techniques as use of internal standards and dilution of sample to give a more uniform matrix. The degree of accuracy obtained is

dependent to a large extent on the time that the analyst is prepared to spend on obtaining good standards and on eliminating interference effects. The standard of accuracy to be obtained is then a matter to be determined by requirements for interpretation of the data and by the costs in time and money. A compromise between these factors is needed for most efficient use of the analytical method.

In the case of soil samples, the variations in minor element concentration to be detected are usually large and thus a relatively low degree of precision will show the same pattern as the most refined method.

Various methods of sample preparation can be used to suit the purpose of the analysis.

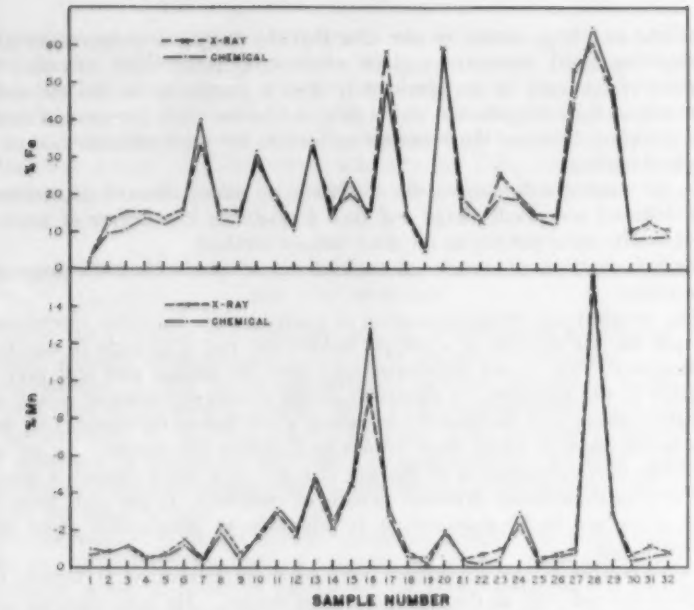
The simplest and cheapest method of analysis with the x-ray spectrometer is to put the soil directly in a sample holder and run it directly in the x-ray spectrometer. The x-ray intensities may then be plotted and will give the variation in the elements. Calibration of the results in terms of actual concentration values may be done by analyzing a number of the samples by some other technique and using these values to calibrate the results. In an area where the bulk composition of the soil changes to a large extent, it may be necessary to standardize different groups of samples. When soils from different areas are to be analyzed, it is advisable to standardize these independently also.

In certain cases the geochemist may be more interested in loosely held metals in the soil than in the total content of metals. He may then use some type of chemical extraction to separate this portion of metal for analysis. Acid and other types of extracts can be analyzed in liquid form on the x-ray spectrometer. This has some advantages and disadvantages as compared to direct analysis of the original soil. An obvious disadvantage is that additional time is required for the extraction process. An advantage is the selectivity the extraction procedure affords. If a very accurate analysis is required, the solution method has the advantage that particle size effects are eliminated when the element is in solution, and matrix effects in general can be minimized by dilution of the sample provided, of course, that the sensitivity of the method is great enough. Internal standards can be added easily in solution with no complications introduced by the mixing problem.

When sensitivity is a large consideration, an extraction technique followed by concentration of the metals in solution by evaporation may be used to advantage.

EXAMPLES OF APPLICATION OF X-RAY ANALYSIS

Instrumental Conditions.—X-ray equipment used in this work was a General Electric XRD-3 spectrometer with a Machlett AEG-50S tungsten target x-ray tube and a G.E. flow counter using a mixture of 90 percent argon and 10 percent methane gas. Soller slits used were either .005° or .010°, depending on resolution requirements or on the convenience of not changing slits. Voltage and current on the x-ray tube was generally set at the maximum rating of the tube (50KV, 50 MA), except where high x-ray intensities made other settings necessary.



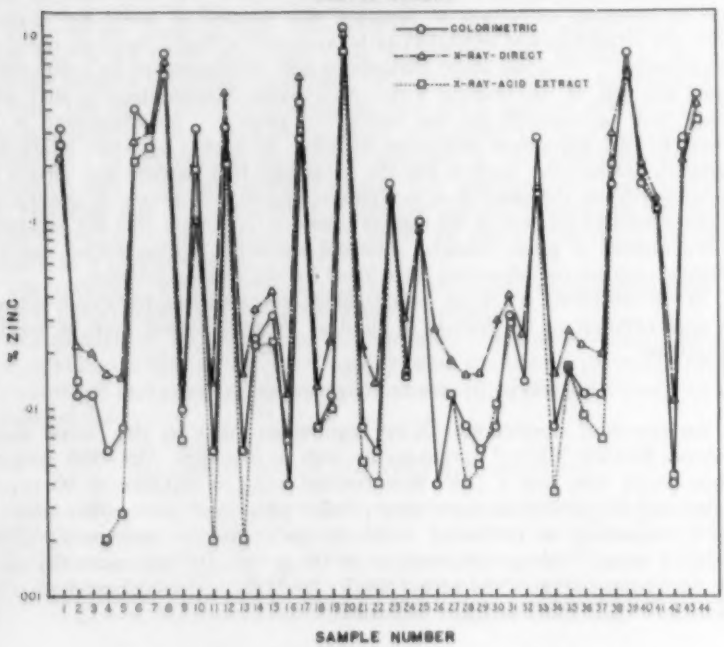


FIG. 2 (top). Iron and manganese in soil samples.
FIG. 3 (bottom). Zinc in stream sediments.

Direct X-ray Analysis for Iron and Manganese.—A series of soil samples rich in iron were run directly for iron and manganese on the x-ray spectrometer. The iron and manganese values for six of these samples were determined on the x-ray spectrometer by a method described elsewhere (4). These six samples were then used as standards to determine the iron and manganese content of the other samples. Comparison of chemical values (determined by acid digestion of samples) with x-ray values is shown in Figure 2. Correspondence of the patterns is good, and direct x-ray analysis appears to be quite adequate for interpretation of the soil pattern.

A word of caution is necessary with regard to the particle size effect. Most of the samples were fine grained as received; however, one sample in particular was considerably coarser than the others. This sample gave an increase in counting rate for FeKα of 62 percent after being ground for five minutes in a mullite mortar. The increased counting rate is in better accord with the chemical results and is the value plotted in Figure 2. One of the fine grained samples was given a similar amount of additional grinding and showed no detectable change in the FeKα intensity. The MnKα peak showed no appreciable change in intensity in either case.

Preparation of Standards for Direct Zinc Analysis.—In order to obtain standards for a group of zinc-bearing soils, several of these samples were analyzed by an addition method of analysis. The addition method of analysis is in common use in optical and x-ray spectrography. As used in this case, a small amount of zinc in the form of a zinc-bearing aqueous solution was added to a portion of a soil sample. The mixture was ground to dryness. The original sample was ground with distilled water for the same length of time to minimize differences due to particle size effects. The sample with added zinc and the sample with no zinc added were both run on the x-ray spectrometer. From the change in intensity with the change in amount present it is possible to calculate the amount of zinc in the original sample. This method of analysis has the advantage that the matrix of sample and standard is the same and the line used to evaluate the relationship of concentration with intensity is the line of the analysis element itself.

Application of the addition method of analysis gave results which are compared with colorimetric analyses made by Mr. H. Dehn, Chemist and Lecturer in the Department of Geological Sciences, McGill University, in Table 1.

This addition method of analysis is preferred to comparison of intensities of the original samples because compensation is provided for the effect of varying matrix. However, the method is more time consuming than direct analysis.

Analysis of Zinc-Bearing Stream Sediments by Direct X-ray Analysis and X-ray Analysis of Acid Extracts.—Results obtained by direct x-ray analysis of a group of stream sediment samples are plotted in Figure 3. These samples are from a metal contaminated area, which accounts for the very high values recorded for many of the samples. Five of these samples were analyzed by the addition method, as described previously, to provide a calibration for the intensity values obtained by running the samples directly.

Also shown in Figure 3 are results obtained by a colorimetric analysis involving nitric acid extraction and an x-ray analysis of the acid extract. In the case of a few samples there was not enough liquid remaining from the colorimetric test and these samples were omitted from the x-ray solution analysis. The solution samples were pipetted into plexiglas holders with mylar covers. Standard zinc solutions were made and used to calibrate the results. Figure 4 shows a working curve for zinc in solution. This figure also shows the effect of the presence of iron in solution on the intensity of the zinc peak. The general similarity of patterns shown by Figure 3 indicates that the same geochemical pattern would be revealed by the three sets of analyses. It should be noted that the x-ray analysis on the extracts is more directly comparable with colorimetric values because these analyses represent readings taken on the extract that was tested colorimetrically, whereas the x-ray readings taken on the original sample would represent the effect of total metal in the sample.

X-ray Analysis by Evaporation of Acid Extracts on Filter Paper.—In some cases the sensitivity of direct analysis is not sufficient to detect low concentrations of metals. In these cases a concentration technique is advisable. A technique which has been found useful is acid extraction of the sample and concentration of the extracted metal on filter paper. X-ray analysis of solutions by absorption on filter paper has been described by Pfeiffer and Zemany (5). They reported good sensitivity for zinc when zinc-bearing solutions were absorbed on filter paper. A modification of the method was devised by the writer. In early experiments, squares of filter paper about one inch in diameter were placed in 50 milliliter beakers, and solutions were evaporated and concentrated on the paper. Good sensitivity was obtained, but the results were erratic. Further investigation revealed that the cause of poor reproducibility was the way the paper curled as it dried. When it curled with the convex side up, a smaller amount of the metal in solution was concentrated on the paper than when it curled in the opposite direction. The technique was altered to use a smaller-sized piece of filter paper in a smaller container, and the tendency to curl was thus eliminated. This also made it possible to concentrate the sample material in the strongest part of the x-ray beam. The containers used were 1.5 centimeter diameter polythene bottle caps, 7 milli-

TABLE 1

COMPARISON OF X-RAY AND COLORIMETRIC ANALYSES

Sample number	HNO_3 extract Zn ppm	$KHSO_4$ fusion Zn ppm	HF decomposition Zn ppm	X-ray
1	200	500	500	570
2	110	120	280	220
3	140	280	400	328
4	40	50	120	90
5	280	600	700	675
6	60	90	140	140

meters deep. The filter paper was Whatman No. 50, punched out into one centimeter diameter discs.

A working curve for zinc is shown in Figure 5. Detection limit is approximately 0.1 microgram of zinc on the paper when the standard solutions are used. The presence of 2,500 micrograms of iron was found to decrease the intensity of the zinc peak to about 36 percent of its former intensity (the test

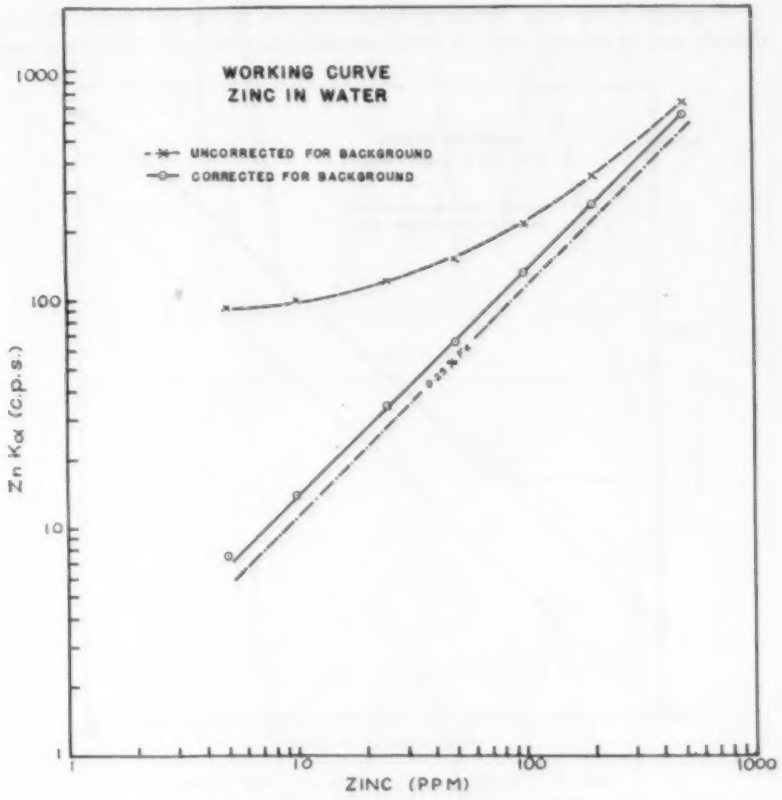


FIG. 4. Working curve—zinc in water.

was tried at a concentration of 500 micrograms of zinc). This concentration of iron is equivalent to 0.25 percent iron in a solution of one milliliter, which was the amount that was evaporated to form the sample. The interfering effect may be compared with the iron interference in solution analysis indicated in Figure 4, since the concentration of iron in the original liquid sample was the same in each case. This comparison shows that, if one starts

with the same liquid in each case, the iron interference is much greater in the case of the filter paper technique than in the case of the direct liquid technique. The reason for this increase in sensitivity to interference is that the bulk of the sample material, which had a tendency to reduce the matrix effect to a common basis, has been removed. The effect of an interfering element (such as iron), which is extracted along with zinc, is then of relatively greater importance.

A group of the same stream sediment samples which had been analyzed directly and by solution analysis were submitted to nitric acid extraction, and

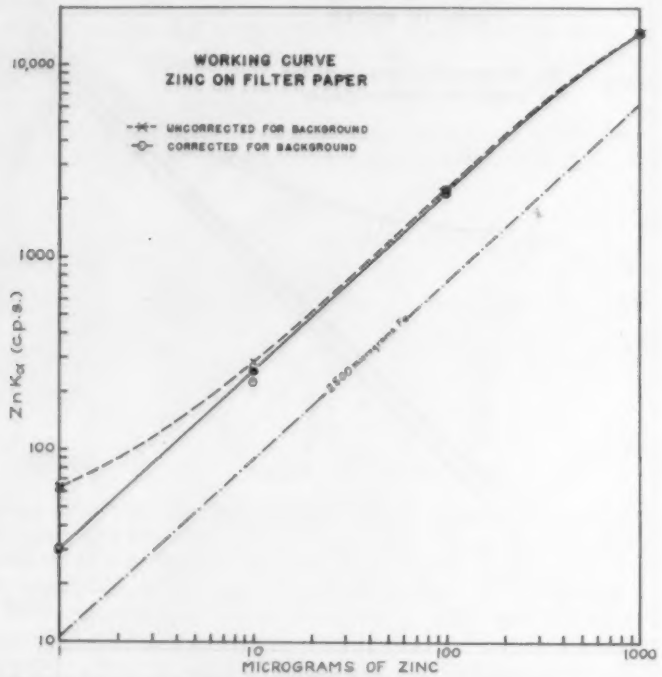
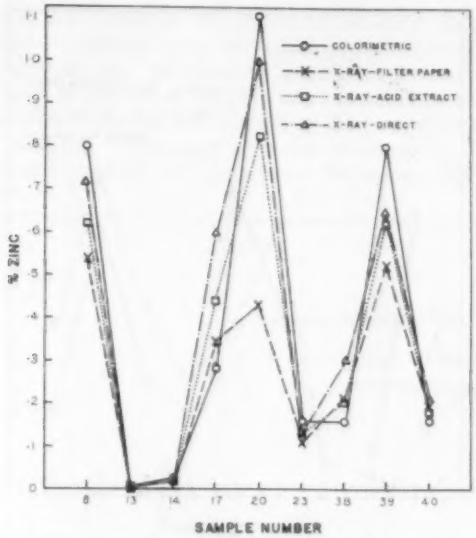


FIG. 5. Working curve—zinc on filter paper.

the resulting solution was evaporated on the filter paper. The correspondence of the results of these analyses with colorimetric results is shown in Figure 6. It should be emphasized that the extraction was separately performed in this case, in contrast to the x-ray solution analysis where the solution was the same extract as used for colorimetric analysis.

The patterns revealed are similar, but the filter paper results are lower in the high concentration range. One possible cause of this is the absorbing effect of extraneous elements in the filter paper samples. Iron is one element



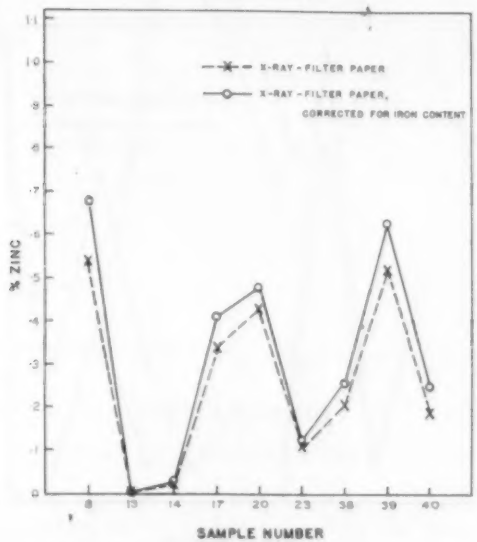
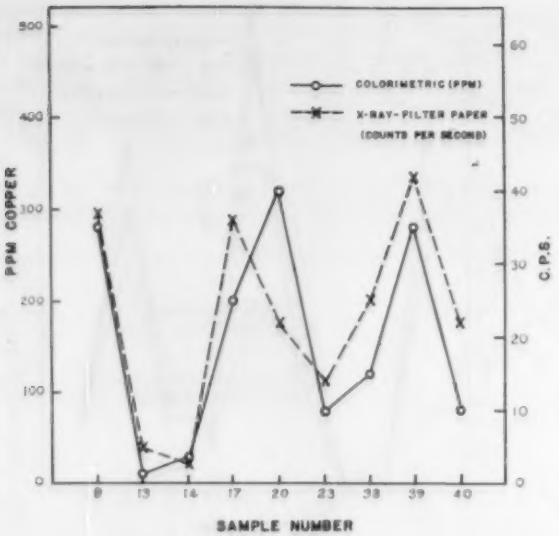


FIG. 6 (top). Zinc in stream sediments.
FIG. 7 (bottom). Zinc in stream sediments, correction for iron content.



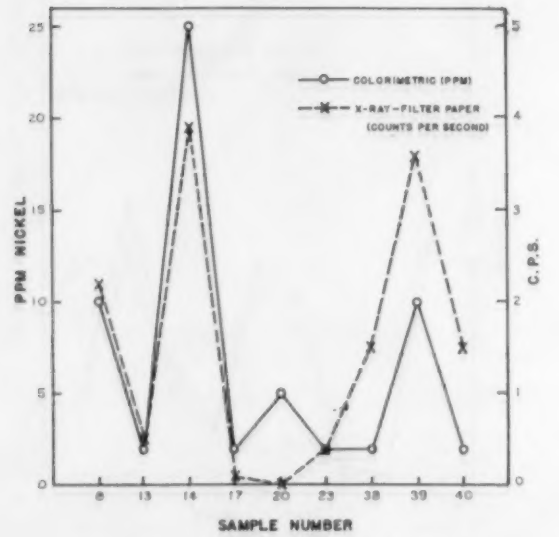


FIG. 8 (top). Copper in stream sediments.
FIG. 9 (bottom). Nickel in stream sediments.

that could have a notable effect in this regard by reason of its relative abundance in the samples, solubility in the extraction process, and high absorption coefficient for zinc radiation. In order to correct for iron interference, the concentration of iron in the actual samples was estimated by means of x-ray analysis and appropriate correction was made to the zinc concentration values obtained for the samples. This result is shown in Figure 7. The corrected values are higher and generally very similar to the values obtained by x-ray

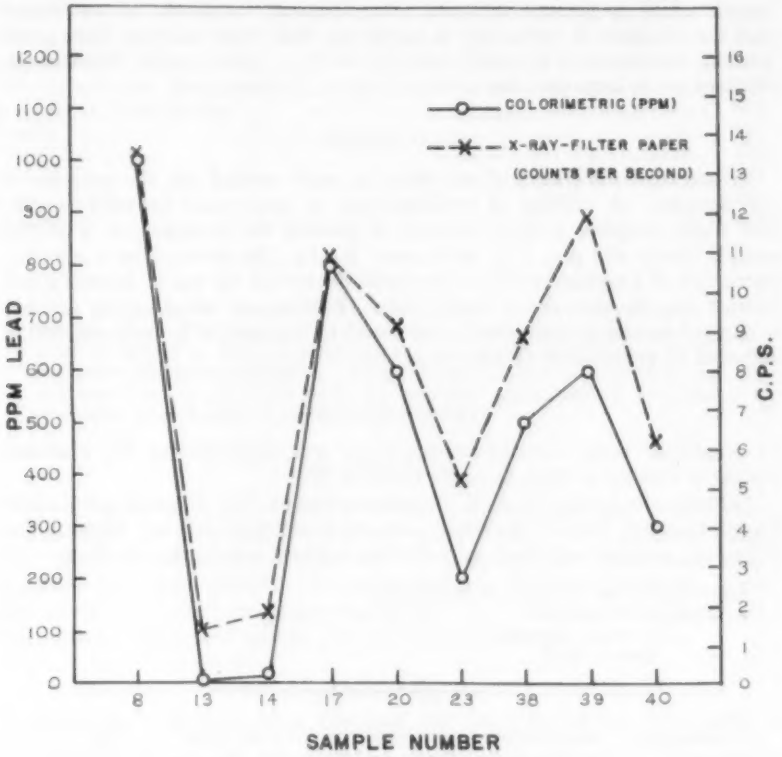


FIG. 10. Lead in stream sediments.

analysis of the solution extracts. The main discrepancy in sample 20 is not removed. The correction shown in Figure 7 alters the general pattern so little that it does not appear worthwhile to make the correction. These soil samples contained iron in the concentration range from 4 percent to 9 percent Fe_2O_3. If iron or some other highly absorbing element was present in very high concentrations in some sample, it might be advisable to make a correction.

Intensities of the CuKα, NiKα and PbLβ_1 were also measured from the

filter paper mounts of these same samples. The counting rates obtained are shown in Figures 8, 9 and 10, along with corresponding colorimetric analyses. Standards were not prepared for the copper, lead or nickel; therefore the counting rate was plotted on an arbitrarily determined scale to correspond approximately with the range covered by the colorimetric analyses. There is a general correspondence between x-ray intensities and concentrations of the elements, with the correspondence being best in the case of lead, which is present in highest concentration in these samples, and poorest in the case of nickel, which is present in lowest concentration. It should be mentioned that the colorimetric nickel test in use at the time these analyses were made was not considered to be satisfactory, so that it is quite possible that the differences are in large part due to error in the colorimetric test.

CONCLUSIONS

X-ray spectrometric analysis offers a rapid method for the analysis of soil samples. A number of elements may be determined on each sample. For many purposes a direct method of packing the samples into a plastic sample holder will give very satisfactory results. In cases where a selective extraction of a certain portion of the metal content of the soil is desired, a soil extract may be analyzed in liquid form. If increased sensitivity is desired, a method involving concentration of metal in the sample by acid extraction followed by evaporation on filter paper may be used.

ACKNOWLEDGMENTS

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McGill University,
Montreal, Canada,
Oct. 1, 1958

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THE GENESIS OF CARBONATE APATITES[1]

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ABSTRACT

A portion of the system Na_3PO_4-$CaCO_3$-H_2O was investigated at low temperatures. The formation of a carbonate apatite by phosphate replacement of calcite in alkaline solutions and the structural positions of the carbonate groups are discussed. Data indicate calcite replacement by low concentrations of phosphate to be the principal mechanism of formation of marine phosphorite deposits.

INTRODUCTION

DURING the course of soil studies at Hanford, it was found that the presence of phosphate ion enhanced the removal of Sr^{90} from waste solution (26). The soils that exhibited this enhanced Sr^{90} removal were calcareous. Consequently the calcite-phosphate-strontium reaction was investigated to ascertain its value as a Sr^{90} extraction mechanism (1). The portion of the study that concerns carbonate apatite genesis is presented here.

LITERATURE REVIEW

The literature concerning carbonate apatites (phosphorites) is voluminous. No attempt will be made to review it in detail. Summaries of the literature on apatites and phosphorite genesis are presented by Jaffe (15), Dietz et al. (7), McConnell (21, 22, 23), Hutchinson (13), Hendricks et al. (12), Pettijohn (28), Arnold (2), Clark (6), and Eisenberger et al. (8).

Mineralogists appear to be in essential agreement that phosphorites are carbonate-bearing apatites. Beyond this point, however, there is little agreement. Hendricks (11) is of the opinion that the carbonate is present outside

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of the apatite lattice as adsorbed or non-crystalline carbonate. Gruner and McConnell (10), on the other hand, presented optical and XRD data to substantiate the location of CO_3^{-2} groups within the apatite lattice. Posner (29) has presented XRD and infrared spectroscopic data that show the carbonate to be present as a separate, admixed phase. Romo (32) demonstrated the absence of hydroxyl groups in a product resulting from the reaction of calcite with alkaline phosphate solutions, and postulated the substitution of CO_3^{-2} groups for OH^- in this product. McConnell and Gruner (25) consider the carbonate to be substituting for phosphate groups, or water and carbonate for calcium along the threefold axes of francolite.

The literature, then, concerning the carbonate of carbonate-apatite appears to be in disagreement on three points; 1) whether the carbonate is present within or outside of the apatite lattice, or as a separate phase, 2) if within the lattice, in what structural position or positions, and, 3) wherever the carbonate is located, how it got there.

To summarize briefly the literature on phosphorite genesis, Murray and Renard (27) postulated the local concentration of phosphate by the catastrophic destruction of phosphatic marine organisms. Blackwelder (3) and Krumbein and Garrels (18) favored low pH (7.0–7.5) and restricted basins for phosphorite precipitation. Mansfield (20) emphasized the role of fluorine in phosphorite deposition, Kazakov (16) the role of CO_2, and Cayeux (5) the concentration of phosphates from sea water by micro-organisms. Dietz, Emery, and Shepard (7) pointed out that the offshore nodular phosphorite deposits of California are found in a highly oxidizing environment. Clark (6) mentioned the origin of phosphorite deposits by the mechanism of differential solution of admixed calcite and calcium phosphates. Bushinsky (4) reported the replacement of calcite and aragonite by phosphate solutions, and the effect of carbonate grain size on the relative rate of replacement. Limestone replacement as a mechanism for the formation of biochemical phosphates was discussed by Hutchinson (12). Irvine and Anderson (13) first demonstrated the replacement of $CaCO_3$ by alkaline phosphate solutions in the laboratory.

The work of Klement et al. (17) on the non-existence of carbonate apatite precipitated from aqueous solutions, and Riviere (31) on calcite replacement by low concentrations of PO_4^{-3} are especially pertinent to this study.

METHODS OF INVESTIGATION

The calcite-phosphate mechanism was studied under equilibrium and non-equilibrium (column) conditions at 28° C. The column setup is shown in Figure 1. This apparatus allows the collection of column effluent fractions at controlled flow rates. Equilibrium results were obtained by shaking aliquots of traced influent solutions in lusteroid tubes along with blank or control solutions, which minimized errors arising from adsorption and decay of tracers. The difference in activity between equivalent volumes of influent and effluent solutions is a measure of the amount of radioisotope removed. It was assumed that there were no differences between the chemical prop-

erties of tracers and corresponding non-radioactive ions. High-salt solutions were sampled and counted on stainless steel plates at secular equilibrium. Calculations were based on differential counting rates to minimize corrections for back-scatter, self-adsorption, and other factors that introduce counting errors between influent and effluent solutions. An open-end, mica-window GM tube, along with appropriate scaling apparatus, was used for sample counting. C^{14} was counted in a proportional gas flow unit.

A Norelco X-ray diffraction unit was used to identify unknown materials.

Types of calcite used included precipitated, optical grade, marble, travertine, and limestone. Except for the physical differences in the above types,

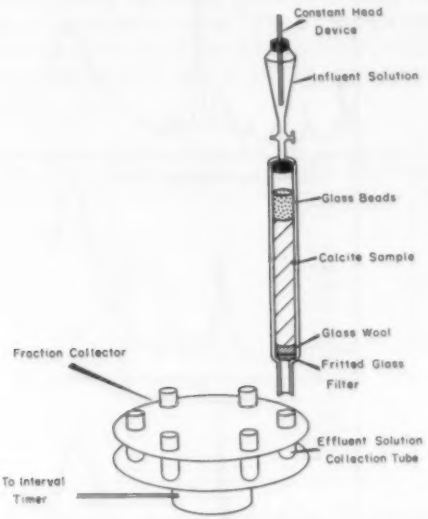

FIG. 1. Sketch of column and collection apparatus used in column studies.

their chemical behavior was the same, and they are all referred to in this paper as calcite.

High-purity radioisotopes from Oak Ridge were added to certain of the influent solutions in amounts convenient for counting purposes. All other chemicals were reagent grade.

RESULTS

A column containing 10 g of precipitated calcite was constructed (Fig. 1) and a 0.3 *M* Na_3PO_4 solution passed over this calcite at a flow rate of 7 ml/hr/cm² and a pH of 12.4. Samples of the calcite were removed at intervals, washed with distilled water, air-dried, and X-ray diffraction patterns obtained. These patterns showed the simultaneous disappearance of calcite

and appearance of an apatite (Fig. 2), corresponding to the idealized reaction

$$NaOH + 3Na_2PO_4 + 5CaCO_3^* \rightarrow Ca_5(PO_4)_3OH + 5Na_2CO_3.$$

Table 1 lists the X-ray diffraction data for the air-dried carbonate apatite of this study.

The phosphate reaction with calcite is a replacement process in the true sense, i.e., the external morphology of the calcite is preserved in the resulting apatite. With the replacement of a synthetic $Ca^{45}CO_3$, the quantitative retention of the Ca^{45} within the resulting apatite was confirmed.

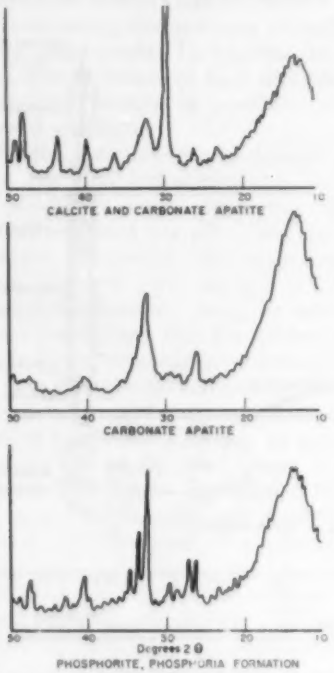

FIG. 2. X-ray diffraction pattern tracings of a calcite-carbonate apatite mixture, carbonate apatite, and phosphorite rock. These samples were air-dried, but otherwise untreated.

To substantiate the assumption that CO_3^{-2} was being replaced by PO_4^{-3} during the calcite-phosphate reaction, a synthetic $CaC^{14}O_3$ was replaced under the conditions of the original calcite column. X-ray diffraction patterns were made from this calcite at intervals (a procedure allowed by the comparatively soft radiation of C^{14}) in addition to C^{14} counting. At approximately 10 percent by weight $C^{14}O_3^{-2}$ in the resulting apatite, the main "d" spacing of calcite at 3.04 Å was no longer discernible. The pattern was entirely that

of an apatite. The structural formula calculated from a chemical analysis of this "apatite" was

$$[Ca_{9.01}Na_{1.12}][(PO_4)_{5.26}(CO_3)_{1.68}](H_2O)_{2.00}$$

Na^+ in Ca^{++} positions balance the apatite electrostatically by compensating for CO_3^{-2} in PO_4^{-3} positions.

A digestion of this same apatite at room temperature in a 0.3 *M* Na_3PO_4 solution for two weeks resulted in an apatite with the formula

$$[Ca_{9.35}Na_{1.07}][(PO_4)_{5.46}(CO_3)_{1.36}][(OH)_{0.67}(H_2O)_{1.33}].$$

The mean refractive index of the above, air-dried sample, was 1.61 to 1.62.

A kinetic study of phosphate removal (Fig. 3) gave a velocity constant, *k*, of 3×10^{-4} per hour per cm^2 under the experimental conditions indicated in Figure 3. Below a concentration of 5×10^{-4} *M*, phosphate removal was no

TABLE 1

X-RAY DIFFRACTION POWDER DATA FOR THE AIR-DRIED COMPOUND $[Ca_{9.35}Na_{1.07}][(PO_4)_{5.46}(CO_3)_{1.36}][(OH)_{0.67}(H_2O)_{1.33}]$

d (Å)	I	d (Å)	I
4.116	W	1.931	M
3.694	VW	1.880	VW
3.402	M	1.834	M
3.138	VW	1.795	VW
2.768	S	1.763	VW
2.687	M	1.721	W
2.607	M	1.500	VW
2.505	VW	1.447	VW
2.232	W	1.371	VW
2.127	VW	1.258	VW
2.055	VW	1.232	VW
		1.216	VW

longer first order. This lower limit is in doubt, however, as influent solutions were not carbonate-free. Under the above conditions, the reaction ceases at concentrations of less than 0.09 ppm (10^{-6} *M*) PO_4^{-3}.

Certain cations that fit into the apatite lattice were also removed by first order reactions (1). These cations may be used to trace the relative rate of apatite formation (the formation of the apatite itself is certainly not a first order reaction). Tracing the rate of apatite formation with Sr^{90}, and adding various concentrations of $NaHCO_3$ to a Na_3PO_4 influent (Fig. 4), demonstrated the influence of bicarbonate concentration on the calcite reaction at 28° C. The HCO_3^- content of the solution affects the solubility of the calcite and, hence, the calcite replacement rate. An increase in temperature from 15° C to 65° C, by lowering the CO_2 content of the system, increased the relative rate of apatite formation by a factor of approximately three. An apatite column, after contact with a solution containing 0.4 *M* $NaHCO_3$, and no Ca^{++} or PO_4^{-3}, yielded an initial calcite that was rapidly dissolved in the same solution.

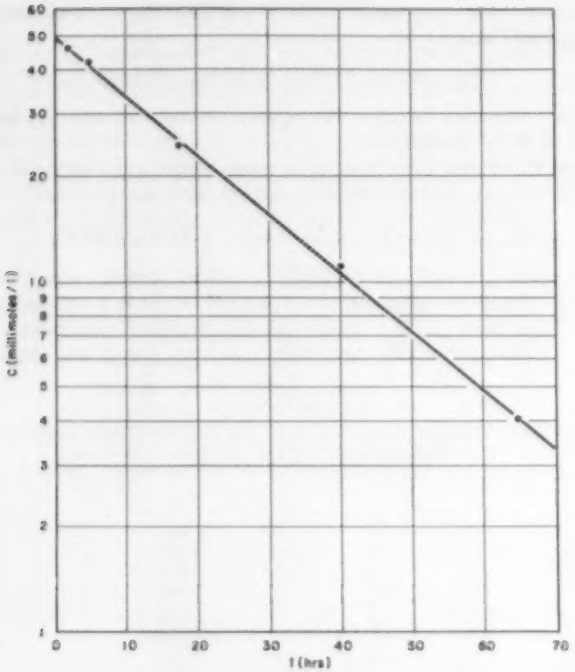

FIG. 3. The removal of phosphate with time during the replacement of calcite by carbonate apatite.

Influent solution: 0.05 *M* $Na_2PO_4 \cdot 12H_2O$, 100,000 d/m/ml P^{32}.	
Influent solution pH	11.8
Calcite weight (mg)	500
Calculated calcite surface area (cm^2)	14.4 ± 1.0
Calcite grain size (mm)	0.077
Temperature (° C)	28

TABLE 2

EFFECT OF CALCITE GRAIN SIZE ON THE RELATIVE RATE OF APATITE FORMATION

Calcite grain size range (mm)	Relative rate of apatite formation (as percent Sr^{90} removed)
1.0 to 2.0	33.9
0.25 to 1.0	36.8
0.05 to 0.25	69.2
0.01 to 0.05	80.0

Solution-calcite contact time (hrs)	1.0
Calcite weight (mg)	400.0
Influent solution pH	11.1

Influent solution: 3 *M* $NaNO_3$, 0.05 *M* $Na_2PO_4 \cdot 12H_2O$, 2 mg Sr $(NO_3)_2$/liter, 100,000 d/m/ml Sr^{90}-Y^{90}; 40 ml solution per sample

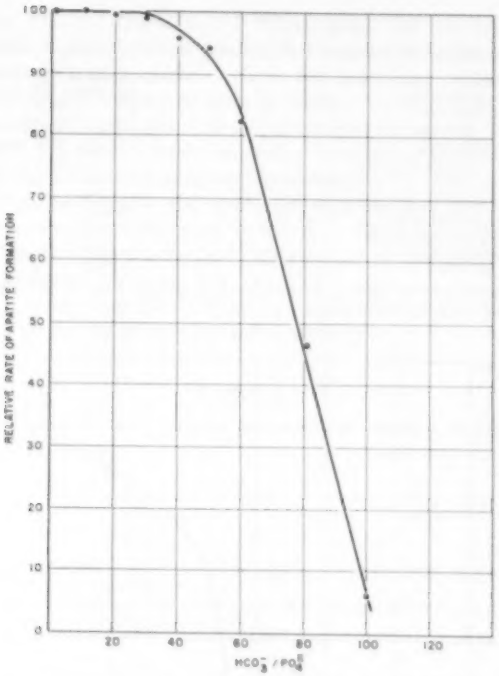

FIG. 4. The relative rate of apatite formation by replacement of calcite as a function of the molar ratios of bicarbonate and phosphate in the influent solution. The replacement rate was measured as the amount of Sr^{90} removed by the replacement process at a fixed flow rate through the calcite column.

Influent solution: HCO_3^- and PO_4^{-3} as above,	100,000 d/m/ml Sr^{90}-Y^{90}.
Calcite column weight (g)	50
Calcite column volume (cc)	34
Calcite column cross section (cm^2)	2.83
Calcite grain size (mm)	1.0–0.25
Flow rate	7 $cc/cm^2/hr$
Influent solution pH	8–9

Calcite replacement by phosphate proceeds when the system is Ca-saturated in relation to its HCO_3^- content, or the degree of undersaturation does not exceed a definite HCO_3^-/PO_4^{-3} molar ratio. The data given in Figure 4 are applicable only for those conditions that are listed there.

The calcite replacement was found to proceed in a 3.0 *M* $NaNO_3$ – 0.05 *M* Na_3PO_4 (pH = 11.1) solution with the same velocity as in a 0.05 *M* Na_3PO_4 solution, when adjusted for pH differences (1). The replacement is little affected by large concentrations of alkalies.

Sr^{90} was also used to show the effect of pH on the relative rate of apatite

TABLE 3

RELATIVE RATES OF APATITE REPLACEMENT OF SOME OTHER CARBONATES

Carbonate	Relative rate of "apatite" formation (as percent Sr^{89} removed)
$SrCO_3$	98.5
$BaCO_3$	96.6
$MgCO_3$	94.8 (wagnerite)
$CaCO_3$ (calcite)	94.4

Carbonate-solution contact time (hrs)	2.0
Carbonate weight (mg)	400.0
Carbonate grain size (mm)	0.01
Solution volume (ml)	40.0
Solution pH	11.1

Influent solution: 3 *M* $NaNO_3$, 0.05 *M* $Na_3PO_4 \cdot 12H_2O$, 2 mg per liter $Sr(NO_3)_2$, 100,000 d/m/ml Sr^{89}-Y^{90}

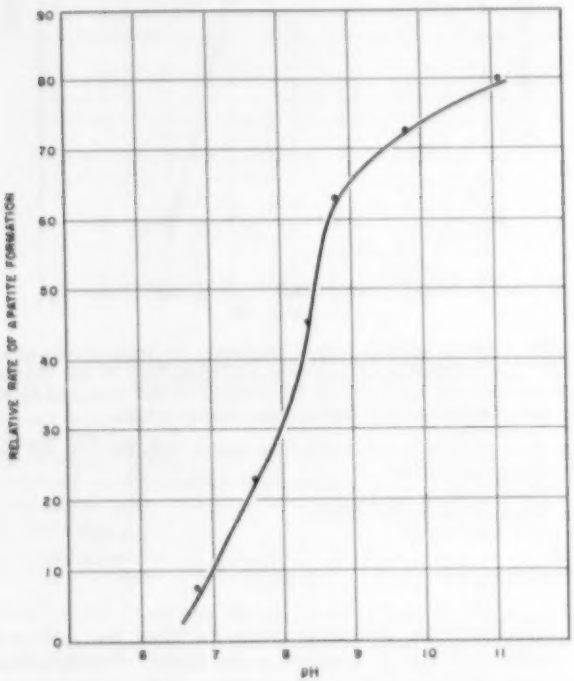

FIG. 5. The effect of pH on the relative rate of apatite formation by replacement of calcite. The replacement rate was measured by the amount of Sr^{89} removed per unit time.

Influent solution: 0.05 *M* $Na_3PO_4 \cdot 12H_2O$, 10,000 d/m/ml Sr^{89}-Y^{90}.	
Calcite grain size (mm)	0.077
Calcite weight (mg)	500
Calcite-solution contact time (hrs)	1.0

formation (Fig. 5), and the effect of calcite grain size on relative rate of apatite formation (Table 2). Abrasion of the larger calcite grain sizes during shaking caused considerable deviation from the grain size ranges as listed in Table 2. However, with equal weights of calcite, the relative rates of apatite formation were roughly proportional to calcite surface areas.

Table 3 gives the relative rates of apatite formation for other carbonates. Note that both the calcite and aragonite type lattices are involved.

Calcite had no appreciable ion exchange capacity for Sr^{90} as illustrated by Table 4. The exchangeability of Sr^{90} for Ca in $CaCO_3$ was investigated to insure that the Sr^{90} used here as a tracer was not removed to any large extent in this manner.

It was also proved that the Sr^{90} and phosphate were not removed from the system as a strontium-phosphate precipitate (1).

TABLE 4

STRONTIUM EXCHANGE CAPACITY OF CALCITE IN THE ABSENCE OF PHOSPHATE

Column volumes	Removal of Sr^{90} (%)
0.98	32.7
1.96	22.1
2.61	10.8
3.92	6.6

Column: 150 g of 1.0 to 0.25 mm calcite, volume = 102.3 cc
Flow rate: 7 ml/cm²/hr
Influent solution: 3 *M* $NaNO_3$, 100,000 d/m/ml Sr^{90}-Y^{90}, pH adjusted to 11.8 with NaOH

As further substantiation that the equilibrium, illustrated by the idealized equation

$$NaOH + 3Na_3PO_4 + 5CaCO_3 \rightleftharpoons Ca_5(PO_4)_3OH + 5Na_2CO_3,$$

apparently lies far toward the apatite side, 150 ml of 0.3 *M* Na_3PO_4 solution containing 100,000 d/m/ml $C^{14}O_3^{-2}$ as the sodium salt was passed through 5 g of precipitated $CaCO_3$ at a flow rate of 10 ml/cm²/hr and a temperature of 28° C. The resulting apatite contained 1,000 d/m/g, or a total of 0.033 percent of the $C^{14}O_3^{-2}$. This small amount of $C^{14}O_3^{-2}$ was probably surface-adsorbed rather than present in the apatite lattice.

Sodium metaphosphate ($NaPO_3$), containing PO_3^{-1} groups linked to form chains by the sharing of two oxygens by each group, was tried as a phosphorus source. No calcite replacement occurred. Discrete PO_4^{-3} tetrahedra were required for the replacement to proceed.

DISCUSSION

The calcite replacement results in a carbonate apatite due to incomplete replacement of CO_3^{-2} with PO_4^{-3}. The reaction equilibrium data and structural formulae indicate that this carbonate can be entirely present in the

apatite lattice when the apatite contains less than 10 percent by weight CO_3^{-2}. Above 10 percent by weight CO_3^{-2}, it is at least partly present as a separate carbonate phase. Structural formulae, equilibrium data, and C^{14} tracing show no indications of the carbonate being present in Hendricks' "voids" (11), or adsorbed to any great extent on apatite surfaces during calcite replacement. $C^{14}O_3^{-2}$ exhibits little tendency for surface removal on apatite in the presence of phosphate concentrations greater than 10^{-6} *M* when present in the influent solution, and no tendency to substitute in the apatite for phosphate or any other lattice position during calcite replacement. The CO_3^{-2} contained in the apatite was present in the original calcite. Apatites precipitated from aqueous solution contained adsorbed $C^{14}O_3^{-2}$ only, as was previously reported by Klement (17), in amounts that were proportional to the $C^{14}O_3^{-2}$ added to the original solution. There is no evidence that an apatite containing structural CO_3^{-2} can be synthesized except by phosphate replacement of a carbonate.

Romo's assumption (32) that CO_3^{-2} groups were substituting for OH^- groups in a carbonato-apatite synthesized under similar circumstances is without foundation in the absence of a chemical analysis. As previously presented results show, it is possible to obtain a carbonate apatite without OH^-. Romo has not shown that CO_3^{-2} groups occupy OH^- positions in his synthetic apatite.

It is entirely possible that Posner (29) has found admixed $CaCO_3$ in a francolite sample, probably representing incomplete calcite replacement.

The variable composition of the apatite phase, even in this relatively simple system, shows the fallacy of attempting to apply the laws of sparingly soluble compounds to apatite. Levinskas (19) also reported that apatites are "solid solutions" and not stoichiometric compounds as evidenced by their highly variable solubility products. The term "carbonate apatite" is used in this paper to designate an apatite that contains 10 per cent or less CO_3^{-2} within its lattice, and does not imply an invariant apatite composition. The term "phosphorite" is used to designate a sedimentary phosphate deposit primarily composed of carbonate apatite.

This investigation has clearly established that the deposition of phosphorite can occur in calcium-free solutions as a carbonate replacement. Furthermore, phosphate is removed from solution by this mechanism at a relatively rapid rate. It is highly improbable that the concentration of PO_4^{-3} could, even locally, rise sufficiently to produce a relatively unadulterated phosphorite deposit in the presence of calcite. Because field studies of phosphorites have shown them to be commonly associated with limestones (7, 9, 12) or limy sediments, the phosphate replacement of these carbonates is considered to be the principal mechanism of phosphorite formation.

The differential solution of limestones, leaving an apatite residue after dissolving $CaCO_3$, is an unlikely source of phosphorites. The average PO_4^{-3} content of limestone is given as 400 ppm by Rankama and Sahama (30), or approximately 720 ppm apatite. Considering a thousand foot column of limestone (density = 174.7 lbs/ft^3) one foot square, containing the above amount of apatite (0.072 percent), the resulting phosphorite residue would

be 0.65 ft^3 in volume. It is impossible to accept differential solution as a phosphorite source when attempting to account for 14-foot beds such as occur in the Phosphoria formation.

Apatite replacement of $CaCO_3$, on the other hand, occurs under conditions that fit the field occurrences and laboratory investigations of phosphorites. These conditions are:

1) a non-depositional environment,
2) limy sediments or limestone, available for replacement,
3) sea water Ca-saturated, or nearly so, in order that the limestone present be in near-equilibrium with the sea water,
4) pH = 7.0 or greater,
5) PO_4^{-3} concentration of 0.1 ppm or greater.

Limestone replacements also can occur during diagenesis of phosphatic shales that contain calcite nodules or layers, or are adjacent to limestones in the sedimentary sequence.

Cyclic replacement of limestone and limy sediments is implied by the results of this investigation. Interrupted limestone replacement, along with the facility of the growing apatite for including other cation such as Mn^{++} or Fe^{++}, can result in agate-like banding characteristic of many nodular phosphorites (4, 7, 22). Replacement, of course, proceeds from the surface of the limy nodule towards the nodule center. The vitreous appearance of certain of the bedded phosphorites (4) was noted on the larger apatite-replaced calcite grains. Fine-grain size calcite cements are more rapidly replaced, due to their larger surface areas per unit weight than are larger $CaCO_3$ crystals. Quartz sand grains and other extraneous material included in the original limy sediments are ordinarily not replaced.

Changes in the chemical composition and crystal size of the apatite do not terminate after limestone replacement is completed. Continued CO_3^{-2} loss and gain in OH^- and/or F are indicated over a period of time.

SUMMARY

Alkaline phosphate solutions were found to replace calcite with a carbonate apatite of variable composition. Relative replacement rates were a function of solution pH, PO_4^{-3} content in relation to HCO_3^- concentration, and calcite grain size (surface area). The carbonate can be present within the apatite lattice, and as a separate phase at greater than 10 percent by weight CO_3^{-2}. There was no evidence for the adsorption of relatively large amounts of CO_3^{-2} by the crystallizing apatite during replacement. Precipitated apatites contain $C^{14}O_3^{-2}$, probably adsorbed, in amounts that are proportional to $C^{14}O_3^{-2}$ concentration in the original solutions. Stability relations in the system Na_3PO_4–$CaCO_3$–H_2O indicate that apatite replacement of carbonates is the most probable mode of formation of large marine phosphorite deposits, due to the operation of the replacement mechanism with PO_4^{-3} and Ca^{++} concentrations far below those required for apatite precipitation.

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RICHLAND, WASHINGTON,
Oct. 15, 1958

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ADDITIONAL DATA ON THE GEOLOGY OF THE MBEYA CARBONATITE

L. J. FICK AND C. VAN DER HEYDE

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ABSTRACT

A discussion of the various geological facts, that have been established during the development of the Mbeya Carbonatite as an economic prospect subsequent to the preliminary investigation by Fawley and James (8) is presented by the authors.

The paper consists of three main parts. A description, based on new fieldwork, of the surroundings of the Mbeya Carbonatite is given by van der Heyde. In it arguments are given for a revised age of the Carbonatite (pre-Karroo instead of post-Karroo), the absence of Rift Valley faults is discussed as in the available evidence concerning the basement structure.

In the second part, written by Fick, a description is given of the phenomena related to the intrusion of the main carbonatite at Panda Hill. Here the salient point, made by the author, is that those rocks which until now were presumed to be part of a volcanic pile are really fenites, i.e., metasomatically altered gneisses of the contact aureole of the carbonatite.

A comparison between the "agglomerates" of Fawley and James (8) and the "Feldspathic intrusives" of Dixey, Smith and Bisset (4) is made in the discussion of the genesis of these rocks the evidence pointing to the existence of "gas-fluxed" system is mentioned. A description of the main carbonate mass and some of its phases and the numerous dike rocks is given.

In the third part, also written by Fick, the minerals occurring in the carbonatite are separately described and their relationship is discussed.

INTRODUCTION AND ACKNOWLEDGMENTS

SINCE the first paper on the Mbeya Carbonatite by A. P. Fawley and T. C. James "A Pyrochlore (Columbium) Carbonatite, Southern Tanganyika" (8), additional field and petrographical information gained, calls for the publication of a revised but still far from complete description.

The Mbeya Carbonatite Complex occupies approximately four square miles and lies at the border of the Rukwa Rift-valley in latitude 8°59′ S and

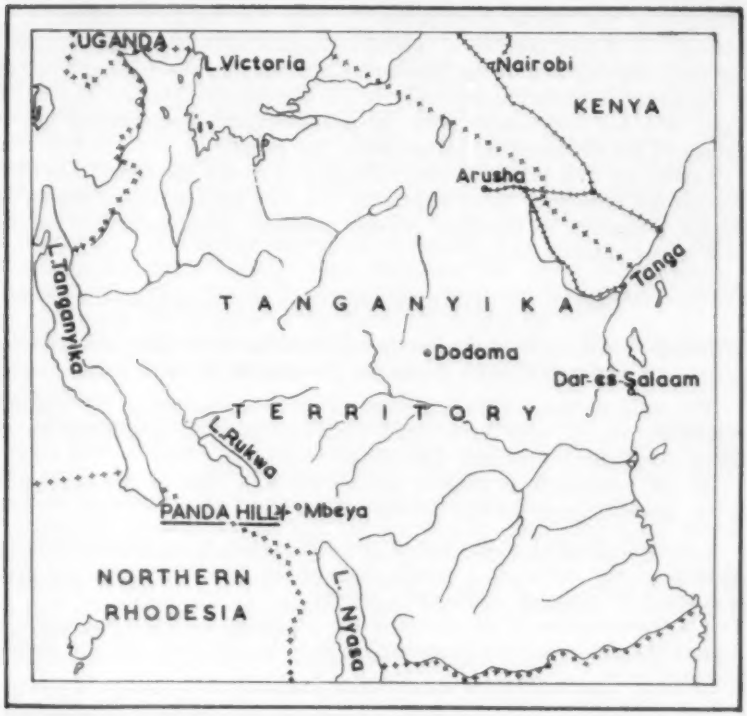


FIG. 1.

longitude 33°14′ E. It consists of two units rising, respectively, 1,100 and 900 feet from the valley floor.

Panda Hill proper, the higher topographical unit, is composed of basement gneiss, fenites and feldspathic agglomerates, intersected by numerous carbonatite dikes.

In the spur leading from the Igale Plateau to Panda Hill, is the carbonatite, which occurs in a slight depression in the spur and is surrounded by altered basement gneisses.

This orebody, a carbonatite plug consisting of about 300 million tons of pyrochlore-bearing carbonatite is being developed by the Mbeya Exploration Company Ltd., jointly owned by the N. V. Billiton Maatschappij, Netherlands, and the Colonial Development Corporation, Great Britain.

As a preliminary to future exploitation a pilot stage has been reached in which mining and milling of the ore at a rate of 200 tons a day has started.

The authors are indebted to the N. V. Billiton Maatschappij and the Colonial Development Corporation for permission to publish this paper; to the Chief Geologist, Dr. G. L. Krol, for his encouragement, and to the General Manager of the Mbeya Exploration Co. Ltd. for his kind assistance. In addition our thanks are due to several colleagues who have been engaged in the field mapping and to the Research Laboratory of the Billiton Company at Arnhem, Netherlands, especially to its mineralogist Mr. A. H. van der Veen, who has collaborated with the petrographical investigations and the writing of the mineralogical paragraph of this paper.

Lastly, we owe thanks to our colleagues from the Geological Survey of Tanganyika, who gave us all assistance, and who have indicated several important references to the East African geology. The discussions we had were highly appreciated.

GEOLOGICAL SETTING OF THE MBEYA CARBONATITE

Introduction and Scope of the Geological Mapping in the Mbeya Exploration Company's Special Exclusive Prospecting License Area

The main purpose of the mapping was a re-assessment of the economic possibilities of the area held under exclusive prospecting license, by the Mbeya Exploration Company Ltd. (Fig. 2).

As the carbonatite is situated on the Western edge of the Rukwa rift valley, this re-assessment was considered to consist of:

a. a determination of the age of the carbonatite, if possible, as this fact might allow the exclusion of certain parts of the area (as these parts might be covered by younger sedimentary series).

b. a determination of the extent of the rift valley faulting—important because of the thickness of sedimentary cover to be expected over the possibly favorable series.

c. as complete a coverage as possible of the remainder of the area, with special emphasis on the area of Sengeri Hill, where a second carbonatite body had been found.

Rock Descriptions

As a result of the mapping investigation, 8 main groups of rocks were distinguished in the S.E.P.L. area. These are (in a chronological sequence):

h Rungwe volcanics
g Travertine and related limestones
f Olive clays and coarse sands
e Cretaceous sandstones

d Karroo sandstones
c Carbonatite suite and contact rocks
b Micro gabbro dikes (dolerites)
a Basement gneiss series

Basement Gneiss Series

The metamorphic rocks found in the area form a fairly complex system in which several distinct types can be distinguished. Predominating is:

Feldspar Augengneiss to Arteritic (Banded) Gneiss.—This rock, which comprises some 90 percent of the Basement system, is quite varied in appearance. In places the ophthalmic texture predominates, at others the banded texture. Many intermediate types have been observed. Mineralogically the main constituents are porphyroblasts of orthoclase, oligoclase, and quartz, and are a "groundmass" of quartz, orthoclase, and oligoclase. Minor constituents are garnet (generally as porphyroblasts), biotite (generally in the ground mass), and some epidote. In some cases the garnet occurs in such quantities (up to 15–20%) that it has to be classified with the main constituents. Microscopic examination showed that quartz is by far the dominant mineral (50–70%)—and dark minerals, apart from garnet, are almost lacking, even though the groundmass commonly has a rather dark color.

Relatively minor types of the Basement system are:

Granulite Quartzite.—This is a very light colored rock with garnet porphyroblasts, quartz to 80 percent, oligoclase about 10 percent, and possibly orthoclase.

Hornblende Gneiss, Garnet Hornblende Gneiss, and Hornblendite.—Apart from the minerals mentioned earlier, common hornblende occurs in the rock. Many different sub-varieties ranging from rocks with about 10 percent hornblende up to almost pure hornblende rocks occur.

Amphibolite.—A special type of hornblende containing rock, found in a few distinct bands of about 1 m thickness, can also be distinguished. It contains no quartz. Hornblende and oligoclase occur in proportions of 6:4. A vein containing hauyne and calcite was found in one slide. This rock may be classed as an amphibolite.

Pegmatite.—Five lenses of pegmatitic texture were also found. They all consist of quartz and orthoclase (macroscopic determination). One of these also contains kyanite.

Marble.—Near the Northern boundary of the investigated area many boulders of marble were found in Cretaceous conglomerates and in river gravels derived from these conglomerates. Unfortunately it was impossible to locate the outcrops of this rock in situ. Most of the boulders examined are a white to pink forsterite marble.

A scarceness of good outcrops, the usually vague boundaries between the types enumerated above,[1] and a lack of time, made it impossible to map these types separately.

[1] Except 4, 5 and possibly 6, relatively minor units.

Structurally the Basement system may be characterized by one major plane of fissility parallel to the banding of the augengneiss with a strike NW and a dip southwesterly of around 45°. However, both steeper and flatter dips of the banding have been found, and near the Western limit of the mapped area, a reversed dip was noted.

Approximately perpendicular to this plane, a system of joints exists (strike NE–SW, dip about vertical).

Linear elements are rarely observed. They consist of a microfolding of the bands in augengneiss—direction of the axis is 135°, dip about 10°—and of a faint linear arrangement of the long axis of the hornblende crystals. Two of these arrangements have been observed, one is roughly parallel to the microfold axis, the other about perpendicular to it, in the plane of the banding (direction SW, dip about 45°).

If the interpretation of the microfolds in the gneiss as dragfolds is permissable, the evidence so far found is that the dips to NE represent parts of the major structure, where the lithological units are "right way up," and where the dip is to SW the units are "overhanging." That is to say the rocks are "younging" to the NE. If this interpretation is correct, there should be a major anticlinal axis of the basement structure not far west of the investigated area. Nothing is known, or can be inferred from our data, concerning the position of the corresponding synclinal axis. No indication has been found to support a hypothesis that more than one structural unit crosses the area.

On the whole these data seem to indicate that the Basement system is a folded, meso-metamorphic sedimentary series. Support for this hypothesis might be obtained from the location and study of the marble mentioned earlier, from a further study and a definite location of the major structural axis in the system.

Micro Gabbro Dikes (Dolerites)

Numerous black, hard, fine-grained dike rocks are found in the area. They generally follow the banding of the gneiss, but in places they cut across the banding. On careful examination chilled margins can be observed. In thickness these dikes range from 2 cm to a few meters. One section examined microscopically shows that the mineral assemblage consists of plagioclase (labradorite) and clinopyroxene (pigeonite ?) in proportions of 6:4, respectively.

Another section (examined by A. H. van der Veen) contains hornblende that may be slightly alkaline, and plagioclase in the andesine to labradorite range. This last specimen may not be truly representative of the group, as it was collected near Sengeri Hill and it may have been altered by the Sengeri Hill carbonatite.

Carbonatite Suite of Rocks

Sengeri Hill Carbonatite.—The only important carbonatite occurrence—apart from the body at Panda Hill (described elsewhere in this paper by

Fick)—is that found at Sengeri Hill. It was examined and sampled during March and April 1956.

The occurrence consists of two important dikes and numerous smaller ones. The most southerly one of the two consists partly of pure carbonatite—the remainder, and also the second dike, is heavily contaminated by numerous inclusions of altered basement fragments.

Of a series of carbonatite specimens from this area a partial analysis was made (analyst J. Trouw) and recalculated in terms of carbonates, although a separate CO_2 determination was not made. These analyses are remarkable for their constant and high magnesia content and their relatively constant proportion of $CaCO_3 : MgCO_3 = 1 : 1$. A direct comparison with the Panda Hill carbonatite is not possible, as this last one is polyschematic in respect to the magnesia content, nevertheless, generally the magnesia content is lower than found at Sengeri Hill.

Contacts are clearly intrusive (cutting the faintly visible banding of the altered gneiss etc.) and the general trend of the bodies is SW–NE. The carbonatite varies in grain size from fine to coarse (½–20 mm), and generally has but few accessory minerals. Of these, pyrite and magnetite can easily be seen—pyrochlore was observed only in an insoluble residue.

The quartz is probably secondary, in places it occurs as distinct veins, elsewhere as vague schlieren (accentuating the flow structure in the carbonatite) and interstitially in the carbonate mass. Barite has also been found in thin slides and residues. The niobium content of these dikes is low—average of 118 chip samples taken at the surface was 0.08% Nb_2O_5.

Contact Rocks at Sengeri Hill.—Though the rocks in contact with the carbonatite are obviously derived from the Basement system, it is equally clear that they have undergone considerable alteration as a consequence of the carbonatite intrusion. Macroscopically the difference between the altered and unaltered Basement is difficult to describe—the main points are: the altered rock has a rusty, reddish color; and the banding and fissility are less distinct than in the normal gneiss.

Microscopically the rock consists of apparently secondary quartz and a main mass of altered (kaolin) alkaline feldspars (orthoclase and albite). The red color seems to be due to limonite. Zeolites were recorded by A. H. van der Veen. No dark alkaline minerals have been observed so far—although Deans (in personal communication to van der Veen) claims to have found some bands containing aegirine in this area.

Small Dikes.—Apart from the main carbonatite body at Panda Hill, and apart from the second body at Sengeri Hill, numerous small dikes of the carbonatite suite occur where the Basement is exposed throughout the entire investigated area. As yet this group defies proper classification, and even the enumeration of the types cannot be attempted as yet. Undoubtedly further investigation (now in progress) will eventually result in a definite chronological sequence being established from the numerous intersections found at Panda Hill and elsewhere.

As far as our data now permit a short description will be given below.

Almost all of the dikes have carbonates as a major primary constituent. Commonly the walls are fairly straight, but when irregularities occur, these can be matched on both sides of the dike, showing clearly that the dikes are of an intrusive dilatational type. The dikes are all very narrow and range in thickness from a few millimeters to one meter. Many show chilled margins and flow banding parallel to the walls, and all types (in places) cut across the textural marking of the host rock. Dikes cutting the main carbonatite masses indicate that the group may be presumed to be younger than the main masses. (The reverse, that is dikes cut by the main masses of Panda Hill and of Sengeri Hill, has not been observed.)

Apart from these features which they have in common, the dikes can be partly classified by:

their mineral assemblage	dikes with and without biotite, feldspar, olivine, phenocrysts are known.
their grain size	medium grained (2 mm) to extremely fine grained types have been found.
their relative ages	many intersections of dikes, which in all other aspects were indistinguishable, have been observed.
the contained xenoliths	the amount of foreign material carried by the dike matrix. Commonly the xenoliths are highly altered, and some signs were observed suggesting that they were being absorbed by the matrix, a process which, if it can be followed to the end—may lead to a completely changed dike material.
the stockworks formed by the different types	indications have been found that, in the main carbonatite body, the different types may form differently oriented stockworks.

In the area surrounding Panda Hill, the principal arrangement of the dikes seems to be imposed by the fissility of the basement gneiss. No conical arrangement, as at Alnö (5) has been observed.

Explosion Vents.—Though, strictly speaking, not dike rocks, the so-called explosion vent breccias consist of highly altered angular and rounded fragments of basement rocks in a matrix of mainly carbonates. They are provisionally grouped in the same class. Their main peculiarity is the fact that the outcrops are roughly circular in outline with a diameter of 10 to 50 meters.

Pure Calcite Dike.—On the Northern slope of Sengeri Hill—just above the Great Northern Road—a very coarse-grained (slightly distorted cleavage rhombohedra up to 5 cm may be obtained) pure [2] calcite dike has been found. Its relation—if any—to the rest of the carbonatite phenomenon is unknown.

[2] 99.8% $CaCO_3$, trace FeO, nil Nb_2O_5, J. Trouw, Analyst.

Fluorite Veins, Quartz Veins.—Crosscutting some of the dikes mentioned under "Small Dikes" are some fluorite veins and quartz veins. Probably connected with these phenomena is the fact that—especially in the neighborhood of Sengeri Hill—parts of the basement gneiss have been completely altered to kaolin.

Karroo Sandstones

Unconformably covering the Basement system, a series of well indurated red conglomerates, sandstones, and mudstones is found in the mapped area. These were identified as the Karroo (possibly restricted to K_2 horizon) on lithological grounds.

Both to the NW (near Igalula) and to the SE near Lake Nyasa, these beds together with coalbearing formations of the same stratigraphical series are known to occur and have been dated (9, 19, 21).[3] The contact between Basement and Karroo is an unconformable one, wherever observed, and the pre-Karroo topography is thought to be the cause of the irregularities of the plane of unconformity.

Cretaceous Sandstones

Again, unconformably covering the previous series, another group of less indurated, also red, conglomerates and sandstones exists—this series is thought to be of Cretaceous age (3).[4]

The unconformity between the above two series is only a minor one —maximum angle between the two is 5–10°.

Olive Clays and Coarse Sands

For completeness sake a series comprising olive silty clays and white coarse quartz sands must be mentioned. This series occurs just north of the mapped area. Its relation, whether conformable or not, to the underlying Cretaceous series, could not be established during the single day spent on their examination. It must be mentioned that Spence (19) gives a description of a similar series resting on the Cretaceous sandstones near the Southern end of Lake Rukwa and resting unconformably on Basement gneisses (quoting from McConnell and Temperly, An. Rep. Geol. Surv. Tang., 1945) much further north. The unconformity between the Cretaceous and this series implied by these observations has been recently confirmed by Brown.[5]

Travertine and Related Limestones

Rungwe Volcanics

The youngest series consists of two contemporaneous parts. One (g) consists of precipitated limestone (travertine etc.), precipitated from thermal

[3] Spurr, A. M. M. (20), verbal communication on a short excursion: C. S. Hitchen expressed as his opinion that the rocks in question might be of K_2 age.

[4] Spurr, A. M. M. (20), verbal communication: D. A. Harkin. N.B. The Stockley and Dixey papers referred to are not available, the references are indirect.

[5] of Geological Survey of Tanganyika—personal communication.

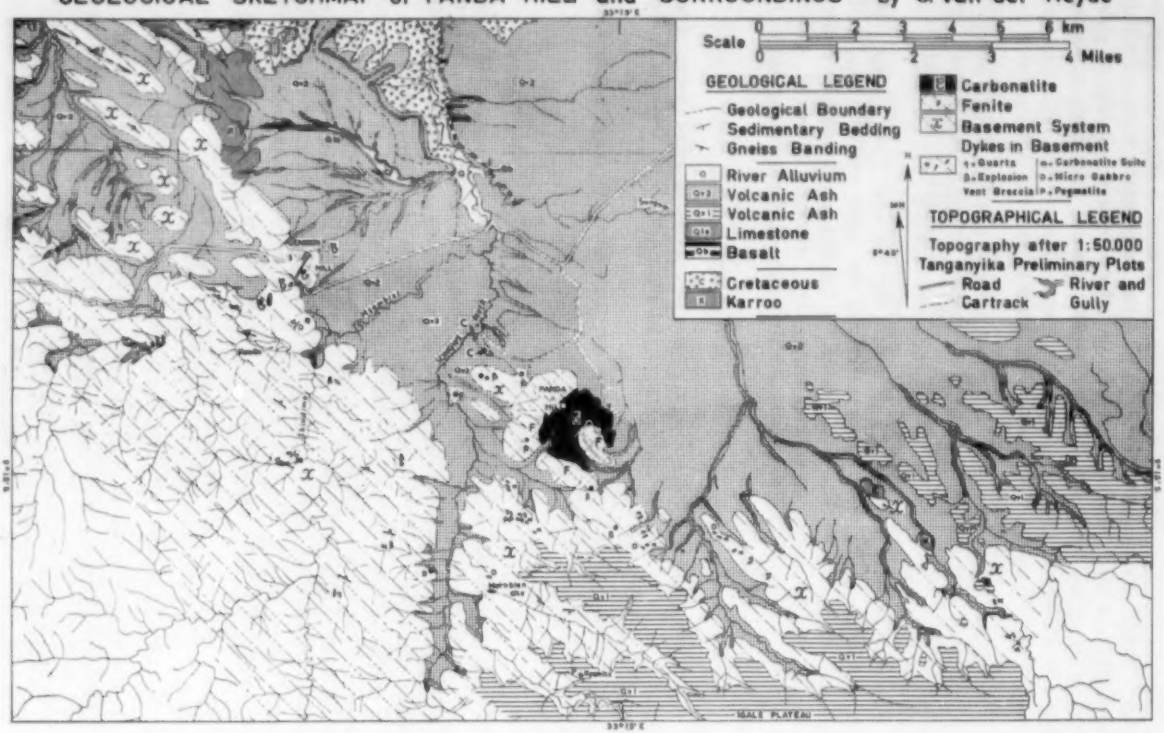

GEOLOGICAL SKETCHMAP of PANDA HILL and SURROUNDINGS by C. van der Heyde
Scale
0 1 2 3 4 5 6 km
0 1 2 3 4 Miles
GEOLOGICAL LEGEND
Geological Boundary
Sedimentary Bedding
Gneiss Banding
River Alluvium
Volcanic Ash
Volcanic Ash
Limestone
Basalt
Cretaceous
Karroo
Carbonatite
Fenite
Basement System
Dykes in Basement
α. Quartz
β. Explosion Vent Breccia
α. Carbonatite Suite
β. Micro Gabbro
γ. Pegmatite
TOPOGRAPHICAL LEGEND
Topography after 1:50.000
Tanganyika Preliminary Plots
Road
Cartrack
River and Gully
MALE PLATEAU

FIG. 2.

springs active till the present day—the other (h) of a series (Qv_2 on sketch map) comprising volcanic ash, with interbedded river gravels, and in the mapped area one olivine basalt flow of great extent.

Possibly significant in respect to this (Rungwe) volcanic series is the fact that in the Southern part of the mapped area (on the Igale plateau) outcrops have been found of a tuff with feldspar phenocrysts. This slightly different part of the series, in which no interbedded gravels were found, had been mapped as a separate unit (Qv_1 on geological sketchmap).

Structure

The "marker" horizons in the area, which are the Karroo and Cretaceous unconformities, were followed as far as possible in order to locate the expected Rift Valley faults. Only slight undulations of these markers were found—these are due to irregularities in the pre-Karroo and pre-Cretaceous topography.

No other indications of faulting were found in the area, except for possibly one exposure where Cretaceous sandstones have a nearly vertical dip. The structure of the Basement system has been mentioned in a previous paragraph.

Chronology

Most data on the chronology of the area have already been mentioned. They are summarized in Figure 3 in which neither the unconformity between the Cretaceous and the olive clays, nor the faulting period that can be inferred from the unconformity are shown. The existence of the third (youngest) period of faulting, shown in Figure 3, was deduced from the fact that the post "olive clays" peneplain has been tilted.

It should be noted that the age of the carbonatite as given in this chronological table differs from the one published by Fawley and James (8). The evidence on which the age determination—given in this paper—is based is found in the following observations: a) a small dike of the carbonatite suite was found to be truncated and to be unconformably covered by Karroo sandstones (Fig. 3) in an exposure 10 km NNW of Panda Hill. b) a dike of the carbonatite suite was found to cut one of the micro gabbro dikes in the area of Sengeri Hill.

James—in personal correspondence—has objected to this age determination, and particularly to the minimum age determined from (a) as he supposes that the truncating formation is Cretaceous in age. The arguments used by him in support of his suggestion are: 1) there is a very great lithological similarity between the supposed Karroo and the Cretaceous; 2) the difference (degree of induration) of the two might be the consequence of a (local) introduction of material.

The first argument is inconclusive, recurrence of a sedimentary facies is a too well known fact to stress this point. The arguments may both be refuted by showing firstly that there are indeed two distinct formations, differing in age, and secondly by correlating these formations with the established stra-

CHRONOLOGICAL TABLE

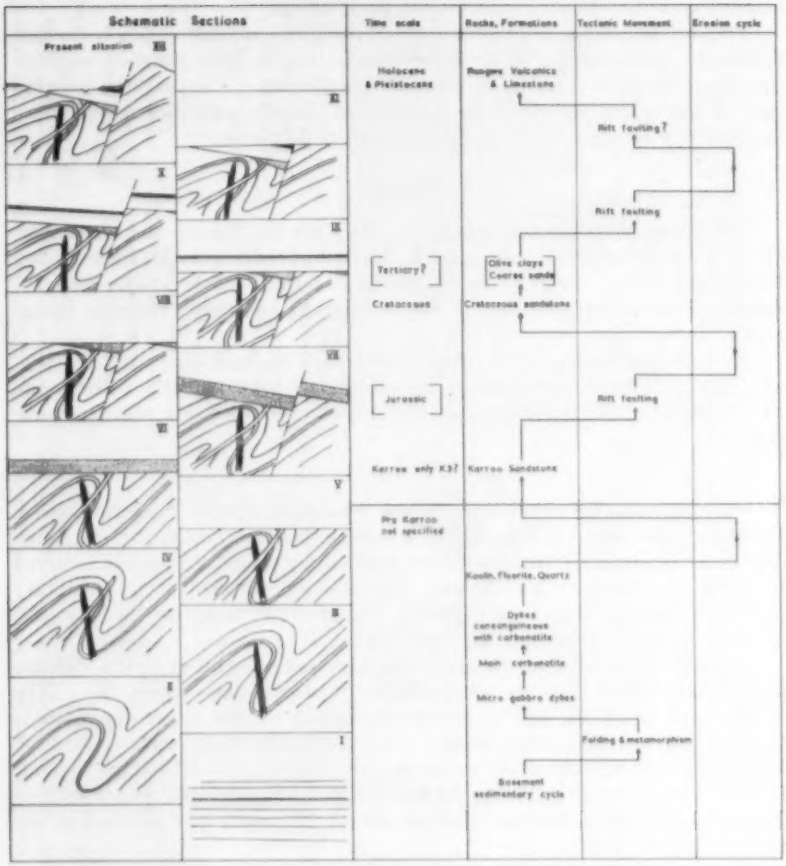


FIG. 3.

tigraphy of the surroundings of the mapped area. Sufficient to show that there are indeed two formations is the fact—as mentioned earlier—that there is an unconformity between the two. The existence of this unconformity can be deduced from: a) the slope of the Chumwa range (just north of the area shown on the map) can be identified as the pre-Cretaceous peneplane; b) this plane may be followed to the South until it truncates the hard formation.

Other facts, which, though not sufficient in themselves to prove a difference

in age of the formations, nevertheless fit better with this hypothesis than with the suggestion put forward by James, are:

1. The abruptness of the transition between the soft (Cretaceous) and hard (Karroo) formations. If James' suggestions were true, we might expect a gradual transition.
2. The fact that the transition is commonly accompanied by a conglomerate in the soft formation. This would be a remarkable coincidence if James' hypotheses were correct—it is a natural consequence if there is indeed a hiatus between the two formations.
3. Then there is the fact that the hard (Karroo) formation is commonly conspicuously jointed, whereas jointing is not observed in the soft (Cretaceous) formation. This fact may be explained by the different behavior in yielding to mechanical stress between indurated and not-indurated parts of the same formation—but it is a simpler solution to suppose that the one formation was stressed and the other one was not, which is: to suppose that the jointing is post-Karroo and pre-Cretaceous.

It is therefore, impossible to ignore the differences between the two formations.

There remains the problem of deducing the ages of each of the two formations. First of all the soft formation. This is known both to the SE (Kiwira Coalfield) and to the NW (Galula Coalfield) to cover undoubted Karroo formations. Its continuity cannot be (reasonably) doubted, nor its extension into Nyasaland. In this last place fossils (Dinosaur remains found by Dixey (3) have proved that its age is Cretaceous. The age of the formation seems therefore well established.

Next, the hard formation. Keeping within the limits of the established fact, we also know that there are but two known formations that simultaneously satisfy the conditions of being older than Cretaceous and having a red sandstone facies. They are Karroo (K_2), Bukoban (a supposed Precambrian formation). We might consider the K_2 age of the hard formation as proved if it were possible to eliminate the Bukoban as the alternative. This is unfortunately not possible from the data.

However, by choosing the correlation of the hard formation with K_2 we obtain the most conservative estimate of the lower age limit of the carbonatite consistent with known facts. A far more promising defence of James' age determination would be to claim, as Dixey, Smith and Bisset do, that the dolerites might be related to and synchronous with the Stormberg volcanics. If that were true, then the fact that the carbonatite is younger than the dolerites would prove James' chronology.

The strength of this defence (of the post-Karroo age of the carbonatite) lies in the fact that there is no direct evidence that can be used to disprove the hypothesis of Stormberg age of the dolerites. However, by examining the consequences of this hypothesis we can show that it would involve rather drastic changes of the interpretation of well established facts of the East African Geology—in other words we may (very nearly) reduce the hypothesis to an improbability.

First of all there is the consequence that if the dolerites are of Stormberg age, then the formation (which I just showed to be older than Cretaceous) must be younger even than the carbonatite dike that post-dates the Stormberg volcanics. The formation would then be post-lower Jurassic and pre-Cretaceous, that is, middle or upper Jurassic, and it would be the first formation of that age reported from inland East Africa.

In the second place if these dolerites should be of Stormberg age, we might expect a series of Stormberg volcanics to exist in the stratigraphic sequence—possibly not in the form of real extrusive volcanics (these might have been eroded during the period prior to deposition of the indurated formation were it upper Jurassic and the erosion period middle Jurassic)—but certainly in its hypabyssal counterpart as dikes in the different Tanganyika Karroo basins. In the geological description of these basins, dikes and sills of possible Stormberg age, are conspicuous by their absence.[6]

Apart from these considerations the supposition of a Stormberg age of the dolerites is not necessary as both Harkin (Songwe Kiwira Coalfield) (9) and Spence (Galula Coalfield) (19) mention dolerites truncated by the Karroo unconformity.

Summing up the evidence and the argument we may conclude that the carbonatite pre-dates a sedimentary formation older than Cretaceous and post-dates dolerite dikes that we may reasonably assume are older than Karroo.

Of James' age determination, the lower limit (pre-Cretaceous) is not definite enough on the available evidence, his upper-age limit (post-Karroo) leads to near contradictions with known facts and must be presumed to be in error. The limits given by me—though possibly conservative as far as the lower limit (K_3) is concerned and very poorly defined as far as the upper limit goes (post-dolerite dikes)—seems the best possible solution under the circumstances. An absolute age determination by lead isotope methods seems highly desirable.

THE CARBONATITE BODY AT PANDA HILL AND ITS ASSOCIATED CONTACT AND DIKE-ROCKS

The Carbonatite

From the surface, quarries, and underground workings a good study can be made of the main carbonatite mass. The orebody mainly consists of white crystalline carbonatite with 80–90 percent calcium carbonate, and may be called a real Søvite. From contact-phenomena and its flow-structure, it is apparent that the carbonatite is intrusive. The flowlines can be observed bending around Basement inclusions. At the peripheral parts of the

N.B. From a strictly logical viewpoint—because it is not the identical dike on which the two crucial observations were made, the conclusion is not warranted. However, seeing how rare carbonatites generally are, it will be agreed that to postulate two (chronologically different) carbonatite intrusion periods is in itself unlikely.

[6] In fact the most Northerly Stormberg volcanics known to me (from the literature) are those of the Chilwa area (Dixey, Smith and Bisset which are not dolerite dikes, but extrusive masses).

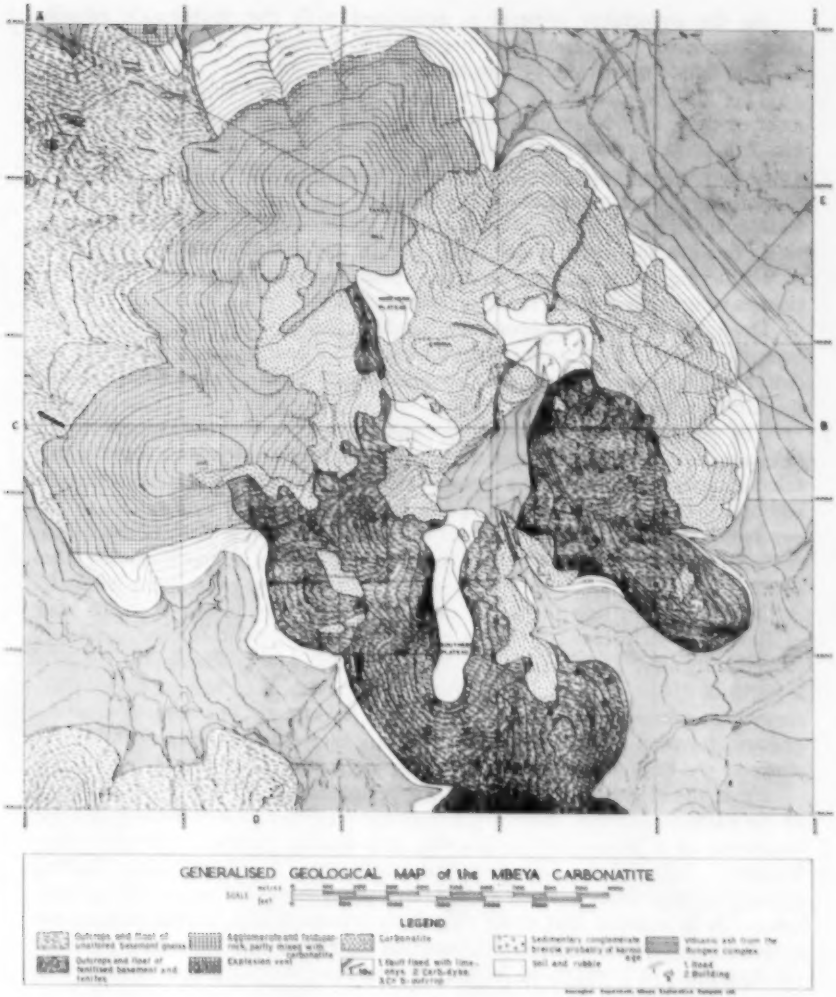


FIG. 4.

plug they trend more or less parallel to the contour lines of the hill. In the center of the intrusion they trend in several directions, and can be followed only over short distances. The flow-banding is visible as streaks of apatite crystals, present in parallel trending flow-planes of varying density. The streaks commonly dip steeply, forming a well marked feature of the igneous limestone.

As the pyrochlore mineral is associated with the apatite-rich streaks, rough estimates can be made of the niobium content of certain parts by examining bands or streaks by means of their flow-lines.

The Mbeya carbonatite has a great variation in carbonate-rocks, and most of them may be regarded as segregations composed of dolomitic, sideritic, and probably ankerite or manganese carbonates. Apart from the dolomite, they never reach great volumes. However, differentiations in types throughout the main plug are very difficult to make, since macroscopically, at least, carbonatite of brown color cannot be distinguished from slightly weathered, fine-grained light bluish-gray, calcitic carbonatite which, susceptible to weathering, takes on a moderate yellowish-brown color, due to limonitization starting from joints, cracks or dike-walls.

Dolomitic carbonatite occurs in irregular masses or in dike-like structures between the calcitic carbonatite. Dolomite is easily recognizable by its "marzipan" outlook. There are also dolomitic rocks, in which microscopically, the calcite mineral is apparent.

The relations between dolomitic and calcitic carbonatite appear to be intimate, as dolomitic carbonatite commonly intersects the flow-lines of the calcitic carbonatite. On the average the former has more quartz and fluorite and magnetite and apatite are much less common, but iron-sulfide-pyrite, pyrrhotite, and chalcopyrite seem to be equally present in both types. Generally, the dolomitic type contains less than 0.2% Nb_2O_5, but if apatite does occur in streaks, assay-values show more than an average niobium content.

At the eastern-side the main carbonatite contains an innercontact zone of Basement inclusions. Starting at the 1,510 m level this zone gradually extends downwards, following the slope of the hill, and reaches approximately a width of 250 m at the 1,350 m level. The clouds of inclusions have an arrangement almost parallel to the flow-line direction. The direction of the gneissic foliation of the separate inclusions is irregular. Some of the inclusions are huge with volumes reaching over 500 cubic meters.

From the clouds of inclusions at the peripheral parts [1] towards the center of the carbonatite-plug, there are frequently observed greenish-black angular fragments of a phlogopitic carbonatite in a matrix of white crystalline carbonatite. Some of the fragments commonly show a faintly visible banding of recrystallized finely grained feldspar in a phlogopitic and carbonatic groundmass. It is believed that these fragments represent highly altered exogenic inclusions. Breccias composed of angular basement inclusions and carbonatite fragments in a matrix of carbonatite are observed along the contacts with the country-rock.

The carbonatite in the neighborhood of the inclusions commonly has been contaminated by obvious assimilation of basement material. The rocks have a pale-blue color and contain the pale-pink xenoblasts of Na-K feldspar. Assay-values show a low Nb_2O_5 content.

[1] As the detailed fieldmapping of the clouds of Basement inclusions along the peripheral parts of the carbonatite plug is not yet completed, these clouds are not shown on the geological map of the Mbeya Carbonatite. The clouds of inclusions shown on the sections are only diagrammatic.

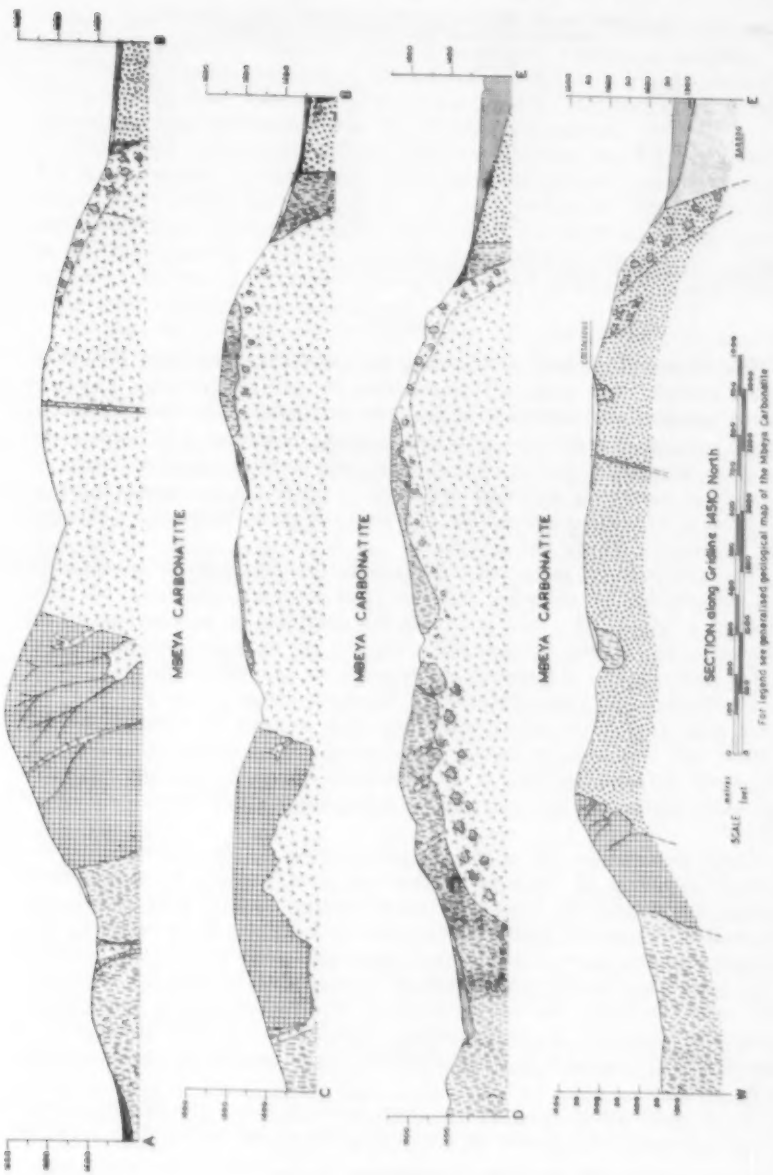

A
MBEYA CARBONATITE
B
C
MBEYA CARBONATITE
D
E
MBEYA CARBONATITE
E
SECTION along Gridline 1450 North
For legend see generalised geological map of the Mbeya Carbonatite

FIG. 5.

A CHEMICAL AND SPECTROGRAPHICAL ASSAY OF THE AVERAGE CARBONATITE FROM THE CENTER OF THE PLUG

	w. %		w. %
SiO_2	5.1	BaO	0.20
TiO_2	0.60	Na_2O	0.1
Al_2O_3	0.78	K_2O	0.1
Fe_2O_3	5.8	Nb_2O_5	0.32
FeO	1.5	P_2O_5	4.2
MnO	0.60	CO_2	31.9
MgO	3.8	F	1.2
CaO	40.5	H_2O+	1.2
SrO	0.33	ZrO_2	<0.1

Research Laboratory, Billiton Co., Arnhem, Netherlands.

Fenites[8]

The Basement gneisses surrounding the carbonatite-plug have been thoroughly altered. The rocks still partly show the gneissic texture. Comparison of specimens of unaltered gneiss with fenitized gneiss shows that the change consists of a decrease in quartz content, hydration of feldspar, forming of microperthite, growth of orthoclase, and in more advanced stages infiltration of calcitic or dolomitic carbonates. As far as our observations go this process is therefore comparable with the fenitization described by Brøgger, von Eckermann, Dixey and others.

The alteration of garnet into phlogopitic pseudomorphs is conspicuous. The introduction of nepheline has not been observed. Aegirine has been found in a "ghost" of a basement inclusion occurring in an apophyse of the carbonatite penetrating the fenitized roof. In any case the alteration of the darker minerals into phlogopitic biotite plays an important role.

Desilication and carbonatization of basement gneiss seems to follow different ways at different points around the plug, at some we observed a calcitization, and at others, we merely found a dolomite-ankerite carbonatization. The width of the altered zone is not completely known, because the surroundings of the carbonatite are covered by volcanic ash and tuffs from the Rungwe volcano.

Large portions on top of the carbonatite-plug can be considered as the fenitized remnants of the original Basement-roof, as they show a gneissic texture, which generally has a direction of foliation parallel to the foliation of the unaltered basement gneiss. These parts are commonly underlain by carbonatite carrying more or less altered basement inclusions. In the fenitized areas there are dike-like occurrences of a moderate yellowish-brown, cherty rock with conchoidal fracturing, some of which may have a great Ba-Sr pyrochlore content.[9] Ba-Sr pyrochlore carrying quartz-siderite rocks of a dike-like habit, in which P. Floor observed baryte are not uncommon in the fenite area.

From observations it is not yet clear, whether these dike-like rocks represent "rheomorphic" fenites or that they have to be regarded as eruptive

[8] The process of alteration by carbonatite intrusions has been called fenitization by Brøgger.
[9] Lit. no. 10

rocks. The latter possibility is not likely, since their counterparts have not been observed in bore-holes intersecting underlying massive carbonatite.

Other fenites are dense, very fine grained Na-K feldspar rocks, containing microliths of iron minerals. Apatite-rich Na-K feldspar rocks carrying quartz, limonite and some Ba-Sr pyrochlore are common.

Field-observations and diamond drill-holes indicate that a gradual process has to be involved, whereby alteration of basement-gneisses was due to emanations accompanying the emplacement of the carbonatite. These emanations may have been metasomatizing in such degree that with increasing amounts of the intergranular fluid the altering rocks became "mobilized." Thence several of the rock types found between the altered rocks with gneissic texture supposedly represent the "rheomorphic fenites."

During the intrusion of the carbonatite the roof of the plug has been stretched, and the resulting cracks may have been filled by rheomorphic fenites.

Feldspathic Intrusives and the Explosion Vent of the Mbale-Zone

At the contact of the carbonatite-plug with the altered Basement gneiss there are feldspathic rocks of various textures. They are well exposed at the eastern and northern side of the Panda Hill proper; many of these rocks have the appearance of breccias and agglomerates composed of closely packed angular or sub-angular fragments of moderate reddish-orange color, and of different types of rocks. The matrix consists of dusky yellowish-brown or light bluish-gray carbonatic material, but a matrix composed of fine-grained feldspathic or silicious substance also occurs. The heavy weathered parts have a tuff-like appearance of dark yellowish-orange and moderate brown colors with spongy surfaces. All the rocks originally (8) referred to as agglomerates and tuffs can be regarded as more or less weathered counterparts of the feldspathic intrusives. They represent essentially orthoclase rocks occurring in a very intimate association with the carbonatite.

Many of the specimens found resemble exactly the description given by Dixey, Campbell Smith and Bisset in their excellent paper on the Chilwa Series of Southern Nyasaland (4, pp. 15–17, 42–43).

Most of the agglomerate fragments are altered basement gneiss, in which the gneissic texture is still visible. Others are of a fine-grained felsitic material of grayish-orange color, in places showing a few euhedral phenocrysts or anhedral porphyroblasts of potash-sodic feldspar. Some of the rocks associated with the feldspathic agglomerates have a scoriaceous habit with tabular feldspar of 3 cm in length. Their groundmass consists of transparent crypto-crystalline material.

There is a great diversity in masses of mixed orthoclase rock and carbonatite, as light colored patches of a lens-shaped habit standing in relief seem to consist of feldspathic carbonatite, and the weathered-out remainder of a more normal carbonate groundmass. Others can be called opthalmic orthoclase-rocks, as they have a fluidal and lens-shaped opthalmic texture. The lenses consist of a slightly porphyritic, felsitic orthoclase mass. The size of the separate eyes varies from 0.1–5 cm. Under the microscope the eyes

have small phenocrysts of orthoclase and a groundmass of anhedral Na-K feldspar. The upper limit of the phenocrysts is 3 mm. In a strongly weathered condition the rocks look like tuffs.

On the small ridge running in a north-westerly direction West of Panda Hill, we found unaltered, grayish-dusky-blue Basement gneiss, cut by an agglomerate band approximately 3 m wide composed of medium orange-pink to light brown fragments of altered basement gneiss. This agglomerate dike runs parallel to the foliation of the basement, in its middle the dike is intersected by a carbonatite dike running in the same direction. At the Bara Bara zone in contact with the white carbonatite, altered basement occurs with gneissic texture gradually changing into a feldspar rock. Both types of rock are commonly found as the components of the agglomerates. From observations in the field it is apparent that the feldspathic agglomerate intrusives are a result of a process together involving basement and carbonatite.

With regard to this problem Dixey, Campbell Smith and Bisset wrote:

> It is very difficult to explain the origin of these abnormal orthoclase-rich rocks. Their very rarity, almost amounting to complete absence, among supposedly igneous rocks is perhaps a clear indication that they are not to be explained as direct products of crystallization from a magma approaching basalt in composition, the crystallization of potash-rich rocks (of which these orthoclase-rocks are extreme examples) could only take place under very special conditions if at all.
>
> It seems much more probable that the orthoclase-rocks are the altered representatives of either a normal igneous rock or the result of alteration of a feldspathic metamorphic rock such as the gneisses of the Basement Complex. Such alteration may have taken place in depth, before the mixed orthoclase-limestone breccias were forced up into the vents, or it is conceivable that at some vents the gneisses were most intensely altered above weak places in the crust where volatiles burst through forming the Chilwa vents, brecciating the altered feldspathic rocks, and drenching them with calcium carbonate. (Dixey and others, 1955, p. 43.)

The explosion vent of the Mbale zone is situated at the contact of outcropping white carbonatite with highly altered basement-gneiss, forming an oval-shaped feature measuring 20 × 8 m. The outcrop of the vent is exposed about 6 m high, having at its base carbonatite and altered basement. On top of the outcrop are rounded and sub-rounded boulders of agglomerate in a calcareous matrix.

There are three kinds of agglomerate, which may merge into each other.

1. carbonatite with oval patches of feldspar
2. carbonatite with pieces of felsitic feldspar
3. "conglomerate" with carbonate matrix, a) boulders of Basement gneiss, b) boulders of felsitic feldspar, c) boulders of orthoclase rock.

The first type is a grayish-brown weathered carbonatite carrying small, oval-shaped feldspathic patches of grayish-pink color, with an average size of 6 × 3 mm. The alignment of the feldspathic spot shows a distinct flow-line texture.

The second type is a grayish-brown weathered carbonatite having sub-rounded, isometric and long pieces of felsitic feldspar-rock weathering out

from the calcareous base. The packing of the felsitic pieces varies considerably. Often they are found in such a density as to leave almost no room for the matrix, but at other places they are less in number. The felsitic fragments have at their weathered surfaces a porous outlook, and they commonly contain several xenoblasts of orthoclase.

The third type of agglomerate is the most conspicuous, it has the appearance of a conglomerate. The fragments are commonly sub-rounded or of more or less spherical shape, though some fragments having long-stretched outlines with rounded edges. They vary in size, mostly less than 15 cm in diameter, but they may be larger up to 0.5 m. Generally, they are very closely packed, leaving room for the matrix at places where their convex outlines are not touching. Each fragment has a dusky brown coat 0.5 to 2 mm in width, the inside rim of the fragments generally has a lighter color, which also seems to be less susceptible to weathering than the nucleus of the fragment. On weathered surfaces the fragments are standing in relief against the more soluble grayish-brown carbonatite matrix.

The boulders consist of three kinds of rock, most of them apparently derived from the adjacent Basement gneisses, still showing a gneissic foliation texture. A nearly equal amount of fragments are of a felsitic feldspathic rock, a much smaller amount of fragments present, forming the third kind, consists of a coarse to medium-grained orthoclase-rock, which not uncommonly shows a trachytic texture. In the interstices between the feldspar crystals are macroscopically observed magnetite, limonite, fluorite, and calcite. In a few cases, small dilution veins of carbonate material fracture the boulders.

At the base of the vent 0.2 m wide bands of massive white carbonatite have enclosed pieces of strongly altered Basement gneiss, faintly showing a gneiss-foliation. The outside of the Basement inclusions is rather frayed and surrounded by grayish-brown feldspathic carbonatite, from which diverge 1–3 mm wide veinlets, intersecting the white calcite carbonatite. Two cross-cutting smaller veins of feldspathic carbonatite intersect both the white carbonatite and the Basement inclusions. Veins of feldspathic carbonatite are conspicuous only on weathered surfaces; on fresh fractures they are more difficult to distinguish from the pale-blue matrix, but recognizable by a finer grain-size and comprising pale-pink orthoclase crystals.

The observations in the preceding paragraphs lead to the following conclusions, which differ from the ideas of Fawley and James on the general structure of the carbonatite.

1. From observations in the field it became clear that the agglomerates and breccias do not represent luted fragments formerly rolled down along a slope of a crater-rim, but that they are intrusive and intimately related with the igneous limestone. Big outcrops at the northern-side of Panda Hill show a vertical banding of the agglomerates, in which evidence of magmatic activity is impressive.

2. Bombs and lapilli, other than from the Rungwe volcanics have never been found. But the Panda Hill agglomerate cannot be considered as the ejectamenta of a volcano, as suggested by Fawley and James (8, Fig. 3);

they are more nearly equivalent to the feldspathic intrusives described from Chilwa.

3. No rocks are known in the area that could be regarded as remnants of a volcanic pile, previously existing at the site, now occupied by the carbonatite-plug. The volcanic material found along the sides and the top of the hill has been identified as being derived from the Rungwe complex.

The genesis of the agglomerates might be interpreted as being caused by gas-fluxed systems, suggested as a geological process by Doris L. Reynolds (17), and which as an industrial process has been named fluidization.

In our opinion such a process is more likely, and detailed study of the agglomerate-breccias will reveal that the agglomerates around the explosion vents represent the equivalent of the agglomerate breccias of Panda Hill. Comminution and attrition by ascending gas-streams makes the diversity of features observed around the Mbeya Carbonatite understandable.

Very recent field-mapping of the agglomerate and brecciated region of Panda Hill proper, led to the discovery of some dike-like carbonatite-agglomerate features, which because of debris covering, are difficult to trace over any great distance. They seem to dip into the hill towards the centre of the main carbonatite plug cutting brecciated basement-gneiss. These features possibly can be regarded as cone-sheets, elements of Crypto-volcanic structures (22) related to subterranean explosions with little or no escape of magma. Gas-fluxing of the basement might have been produced by the magma of which the cone-sheets were filled.

Dikes and Lime-onyx

The main carbonatite is intersected by numerous dikes. Apart from dolomitic dikes, typical calcitic dikes with calcite of two generations, the oldest of which are turbid and iron-stained; alvikitic dikes carrying Na-K feldspar laths have been observed. Dike-rocks containing forsteritic olivine, or olivine totally replaced by calcite, are also present, but this list is probably still incomplete.

The greater part of the dikes have suffered severe decomposition and have been changed to a soft limonitic sand. Weathering of dikes may have a bearing on the adjoining carbonatite, which then weathers at the same time, giving rise to cavities of different sizes more or less running along the strike of the dike. In the less decomposed dikes flow-line banding and chilled margins at the walls could be examined.

It seems possible that there exists a conical arrangement of the alvikitic and of some of the dolomitic dikes in the carbonatite-plug, but examinations thereon are not sufficiently advanced for such observations to be conclusive. As mentioned in the first chapter we found no conical arrangement of the dikes surrounding the Mbeya carbonatite. This seems to imply that their emplacement has started from a much higher level than at Alnö, or that the erosion level at the Mbeya plug is deeper than at Alnö, which is not likely since a part of the former still has its fenitized roof.

The dike-rocks mostly have a very low pyrochlore content. Spectro-

graphic assays of core-samples reveal that a greater part of the cross-cutting dikes in the carbonatite have a high BaO content (more than 0.5%). In literature on carbonatites, great emphasis has been laid on the BaO : SrO ratio. At the moment we have an insufficient number of assays on which both BaO and SrO have been determined, but the assays available show that the Mbeya Carbonatite has a marked preponderance of SrO over BaO (BaO : Sro = 1 : 3), whereas most of the younger dikes show a preponderance of BaO over SrO, but there are other dikes showing a greater SrO content than BaO.

It would be of great interest from a petrogenetical point of view to extend the spectrographical assaying of rock-samples, as dikes and hybrid fenite rocks generally are too fine grained and weathered to use the microscope successfully.

Fawley and James (8) mentioned the occurrence of banded travertine filling the fissure of a large fault. Since then several faults have been found, of which the larger ones are filled with lime-onyx, as we prefer to call the banded fillings consisting of younger calcite.

The walls of the faults generally carry brecciated carbonatite accompanied by a clayish fault-gouge. Sometimes we observed brecciated lime-onyx cemented by onyx-marble in the middle of the faults. Onyx-marble contains no Nb_2O_5.

Sandstones

Near the top of the main carbonatite in drill-holes and in Adit I, two occurrences of a conglomerate-breccia have been found. They consist of fragments of sandstones and rounded quartz pebbles, embedded in a reddish-brown matrix consisting of medium grained quartz. The shape of the sandstone pockets in the carbonatite, as proved by drilling, make it certain that the pockets represent sandstone filled pot-holes. The age of the conglomerate-breccia is thought to be Cretaceous.

At the foot of the carbonatite hill near Adit II, two drill-holes found a dusky-red, rather fine-grained sandstone, covered by volcanic strata of the Rungwe. At a vertical depth of 11.5 m one drill-hole reached the carbonatite after intersecting a 1.1 m. wide contact-rock composed of brecciated pieces of white and brown carbonatite, and recrystallized quartz-feldspar basement, embedded in a base of dense limonitic material. A few meters from this bore-hole a trench was dug, in which were exposed carbonatite, a basement-carbonatite breccia, the above mentioned contact-rock, and the sandstone. This trench showed that the outermost rim of the sandstone has been brecciated also, the matrix being the same as from the contact-rock.

The sandstone is thought to be Cretaceous, although it is difficult to be sure, as Cretaceous and Karroo sandstones of some layers have a great similarity. The peculiar contact-rock can be interpreted as a fault-rock, and no conclusions are made with respect of the relative age of the carbonatite.

On the top of a small hill near Mill site II occurs an agglomerate-breccia composed of Basement fragments in a dense, dark yellowish brown, mudstone-like matrix. This matrix also contains small comminuted Basement-grains, and the breccia resembles in every respect the basal "conglomerate" of the

FIG. 6. Top is Karroo basal conglomerate (c); left and right is basement gneiss (G); center is carbonate dike.

Karroo-Basement contact found by van der Heyde, at a distance of 7 miles from Panda Hill.

Surface Detrital and Sink-holes

Large parts of the carbonatite are covered by residual limonitic soil and carbonatite debris, and at places with outcropping Basement nearby, the debris consists of basement-rubble. Commonly, the surface detrital has a thickness varying from a few decimeters to 1.5 meters, but at the center, where the contours of the ground favor water concentrations, its thickness may reach 10–15 m.

As already stated by Fawley and James, the surface detrital shows a niobium content twice as much as that of the underlying carbonatite. However, at places where surface detrital has been covered or mixed with volcanic ash from the Rungwe, the values are much lower.

The carbonatite surface appears to be roughly etched. Outcropping above the soil are large pinnacles of carbonatite, and below the detrital are many

funnel-shaped solution-holes, which might continue into cavities tens of meters downwards. Most of the sink-holes between the pinnacles however are filled with soil and decomposed rock. They commonly contain slightly weathered euhedral pyrochlore crystals, which are apparently liberated by solution of the carbonatite. The influence of the sink-holes on the rock rapidly diminishes at a depth of 4–6 meters from the surface.

MINERALOGY OF MBEYA CARBONATITE

Many minerals are found in the concentrates, tailings, slides and polished sections. Between several minerals the relative age relations are fairly well known, between others they must still be studied.

In the concentrates are sphene, ilmenite crystals, reddish garnet ($n \sim 1.77 - 1.78$), an unknown mineral with the following properties: birefringence $0.035 - 0.040$; $n = 1.69 - 1.71$; $c/n\gamma = 48°$; $2V$ = very small, pyroxene mean cleavage; density > 3.3; color (seen under binocular stereo microscope) dark green (clinoenstenite variety?) (23).

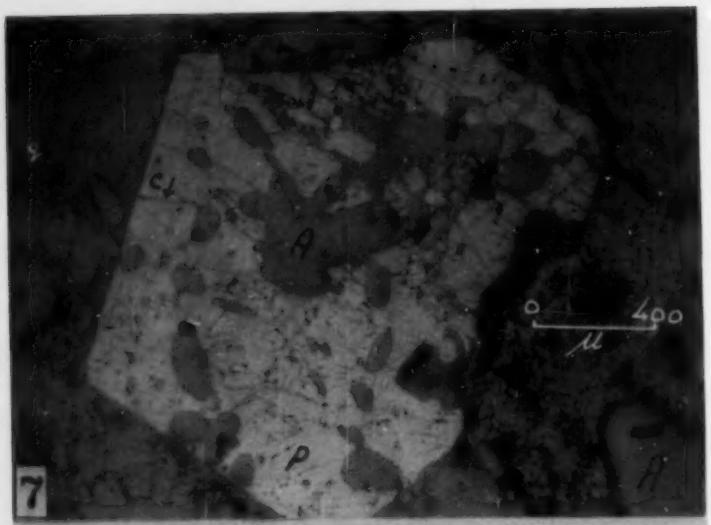
In polished sections, slides, concentrates and tailings the following minerals are observed.

Pyrochlore.—This mineral occurs in such quantities as an accessory mineral that the Mbeya Exploration Company Ltd. has been formed to explore the possibilities of mining the carbonatite for its niobium content. The most common type is grayish-olive to olive-gray, but all shades from dark brown to yellowish-gray may be found. The mineral is associated with apatite and magnetite. The crystal form of the mineral is commonly an octahedron. In fact it is a combination of an octahedron and a hexahedron. Pyrochlore may be replaced by apatite, carbonates, rutile, goethite, quartz, and other minerals. In places it is so extensively replaced by calcite that its original euhedral shape is totally lost. In carbonatite dikes calcite pseudomorphs after pyrochlore with only rudimentary pyrochlore fragments of submicroscopic sizes are found.

Euhedral inclusions of apatite and rutile are often found in pyrochlore. Rutile may be replaced to some extent by pyrochlore. In polished sections are some euhedral crystals with a strong yellow internal reflection. The mineral has reflectance a little lower than pyrochlore and a hardness much higher than the last mineral. The shape is that of a rhomb. It may be more or less replaced by pyrochlore. This mineral is probably sphene. Some pyrochlore is replaced by zircon. Examinations of slides and polished sections show that in the sequence of crystallization, the apatite is partly older, partly syndronous and partly younger than pyrochlore.

In phlogopite-meroxene fenites a pyrochlore with an imperfect structure is found. The high Ba and Sr content, the lack of Ca and Na in this mineral and its relative high parameter of 10.562 Å is striking. Details about this mineral will be published by E. Jäger, E. Niggli and A. H. v. d. Veen (10).

Calcite.—Calcite normally occurs as a granulated mass of anhedral crystals and is sometimes found with sizes up to 1 cm. Rhombohedral cleavages and



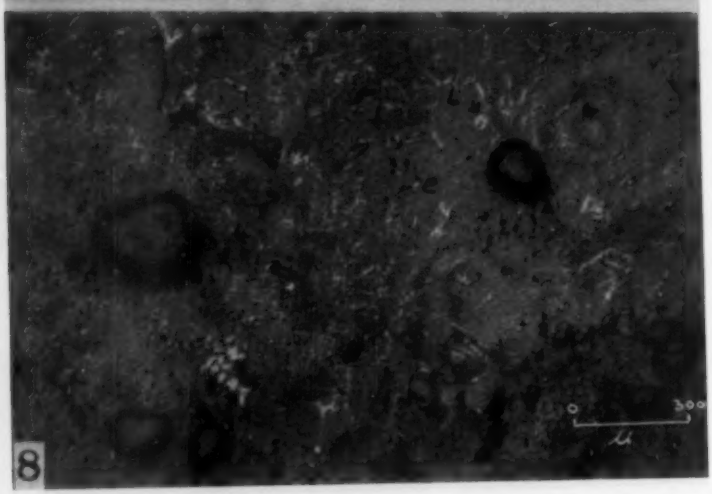


FIG. 7. Pyrochlore with many apatite inclusions, found in a limonitic carbonate dike of the Museum zone; reflected light. Gray, apatite (A); gray and dark gray, carbonate (c); light gray, pyrochlore (p); dark gray (mostly with some relief), quartz (q); black-pits etc.

FIG. 8. Limonitized carbonate rock, limonitic carbonate dike of the Museum zone; reflected light. Gray and dark gray, carbonate (c); light gray to nearly white, limonite (goethite, L); dark gray (with relief), quartz (q). The mineral marked F cannot be further defined. It is probable carbonate. Black-pits etc.

polysynthetic lamellar twinning are commonly observed. Calcite may occur in several generations, of which the older ones may be very cloudy. This is due to fine opaque or nearly opaque inclusions, gas-bubbles and so on. The mineral has replaced nearly all of the other minerals to more or less extent, but calcite may have been replaced by goethite and quartz.

Calcite occurs in cavities, geodes, or cracks as euhedral rhombohedral crystals. Commonly carbonatite fragments show a clear reddish fluorescence in short wave ultra violet illumination. This is probably due to some $MnCO_3$ in solid solution.

Dolomite.—This mineral generally has a finer grain size than calcite and a vitreous luster; rocks containing dolomitic carbonates have a typical sugary appearance. Related varieties such as ankerite-magnesite are not clearly proved, since staining tests showed no definite results (except probably the Alazirine Red S test; this test will be tried in future). The MgO content of the rocks can easily be proved by the Magneson I test. The mineral siderite is not yet clearly proved.

Apatite.—This is the most common accessory mineral in the carbonatite and some of the fenites. Generally the mineral has a nearly euhedral appearance. The crystal-edges are mostly more or less "round off," so that the grains may attain more elipsoidal habits. Needles (perhaps rutile), "negative crystals" filled with liquid and gas, inclusions of indefinite shape, carbonaceous matter, and fluorite are commonly present in the apatite crystals, and are generally directed along the c-axis of the apatite crystal.

Megascopically the apatite is mostly colorless but it also has pink, reddish and very pale green hues. Analyses performed at the Research Laboratory of the N. V. Billiton Maatschappij at Arnhem showed that this apatite contains about 1% Ce_2O_3 by weight.

Apatite is closely associated with pyrochlore. There exists a statistical significant correlation between the Nb_2O_5 and the P_2O_5 content of the drill cores. The higher the niobium content the higher the P_2O_5 percentage. The observed correlation:

$$M\ \{y/x\} \sim 3.47 + 3.54\ (x_1 - 0.331)$$

with x_1 the Nb_2O_5 percentage of the sampled drill core. The correlation coefficient $r_{xy} = +0.5264$.

In the carbonatite, segregations are found in which apatite occurs as oval shaped patches. This is also described by W. C. Brøgger (1) in the rocks from Fen in Norway. The apatite patches have long stretched shapes commonly 1–2 cm long and 0.5–1 cm wide and perfectly rounded outlines, which are dented at one long side. These patches are close together, and lined up in streaks, with fine limonitic veins banding round the apatite lenses. These features give the rock a distinct fluidal texture. The lenses are composed of numerous apatite-needles 0.03 mm thick and lengths of 0.1–1 mm.

Magnetite.—This mineral occurs in disseminated octahedrons with diameters of microscopic sizes up to several centimeters. In reflected light

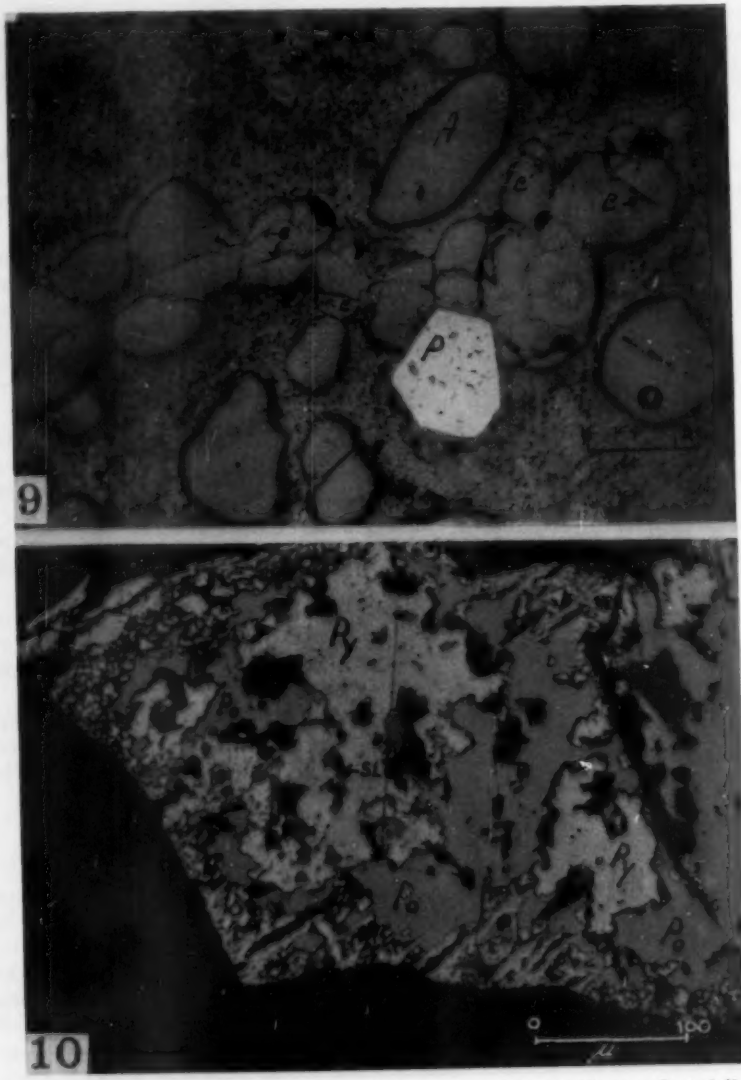


FIG. 9. Part of an apatite schliere, limonitic carbonate dikes; reflected light. Gray, apatite (A); gray to dark gray, carbonate (c); light gray specks, limonite (L); dark gray (mostly with relief), quartz (q); very light gray, pyrochlore (p); black-pits. Note the oval shape and the rounded outlines of the apatite crystals. To a small extent apatite is here replaced by quartz and carbonate.

FIG. 10. Pyritized pyrrhotite in carbonatite rock of the Museum zone, reflected light. Gray, pyrrhotite (Po); light gray, pyrite (Py); dark gray, sphalerite (sl); very dark gray to nearly black, gangue material; black-pits and cracks in the section.

exsolution lamellae of ilmenite, partly altered to rutile and/or leucoxene, can be observed. Magnetite is commonly partly or totally altered to hematite (martitization) and limonite (mostly goethite). At several places there have been found dike-like features, composed of magnetite and pyrochlore, the interstices between the crystals being filled with apatite. This type of rock may contain Nb_2O_5 up to 4.5%. Apatite inclusions may occur in magnetite or its derivatives. The mineral may have been replaced to some extent by carbonates.

Pyrrhotite.—The mineral is found throughout the carbonatite. It may be more or less completely replaced by pyrite, marcasite, and limonite. It appears that the pyritization of the pyrrhotite occurs to a much less extent in the more dolomitic parts of the carbonates.

In a few places an intermediate product between magnetic pyrite and marcasite is observed. This mineral is strongly anisotropic with colors like those of marcasite. This intermediate product is also described by Ramdohr (15) and others.

Chalcopyrite also occurs as an inclusion in pyrrhotite, and sphalerite as inclusions in pyrite. These two minerals are only rarely observed in the carbonatite rocks.

Galena.—This mineral is seldom present. In polished section it is observed replacing pyrite, calcite, and pyrochlore.

Quartz.—Quartz occurs in younger veins and druses to a minor extent scattered in the carbonatitic rocks. Dolomitic carbonatite certainly carries younger quartz than the calcitic carbonatite. Quartz replaces many other minerals occurring in carbonatite such as pyrochlore or apatite in various degrees.

Opal, Chalcedony.—In the more or less silicified carbonatites and fenites much opal and some chalcedony is found. The color of the opal is milky white or brown to nearly black (due to numerous nearly submicroscopic inclusions of goethite and hematite). X-ray powder photographs of the white opal show many weak lines, which are probable indications of quartz and cristobalite. Microscopically the white opal shows distinct "tension crosses" between crossed nicols and a very weak anomal birefringence.

Feldspar.—Rarely some feldspar is found in the carbonatite; mostly this is orthoclase, but there is also some albite found.

Fluorite.—The mineral, deep violet to colorless, is commonly associated with the younger quartz.

Barite.—This Ba-sulfate occurs in some slides and concentrates.

Collophane.—This phosphate sometimes is found as a waxy coating in joints.

Mica.—A reddish-brown biotite seems to be commonly present in the calcitic carbonatite, but it occurs only in greater quantities at certain very limited places, with sizes up to 5 mm across, but mostly smaller. The measured optical constants of this mineral are as follows:

n_x = red-brown
n_y = light brown
n_z = very light brown to colorless

$-2V$ = about 9–10°
n_y = about 1.61 – 1.615
n_z = about 1.620

Mr. van der Plas recorded in an unpublished report [10] biotites with about the same pleochroism and n_z, $a - 2V = 0°$ to 8°; birefringence = 0.040. Borax bead test with an oxidizing flame gives an amethyst blue bead (Mn!); X-ray powder photograph indicates a mineral between phlogopite and eastonite. The above stated properties point to a mineral much resembling a Mn-rich biotite variety described by J. Jakob (11).

Mr. van der Plas described also a milky white Li-mica (microscopically a dense aggregate) that he found in a carbonatite sample. He obtained the following properties for this mineral: mean index of refraction between 1.553 and 1.559; colorless to light-violet in thin section; flame test points to Li. These stated properties point probably to a lepidolite variety. Phlogopite and meroxene are found in the fenitic rocks. The Mn-biotite may be considerably altered and replaced by carbonate. Observed alteration products are chlorite, limonite, pyrite, and probably rutile and/or ilmenite.

Cassiterite.—The occurrence of this mineral has been recorded by several geologists, who have studied thin sections and samples of the Mbeya carbonatite rocks. Mr. van der Plas has confirmed this finding.

Amphibole.—This mineral has been recorded by Fawley and James (8), James and McKie and van der Plas. Fresh crystals occur probably only in minor quantities. Mostly they were strongly altered (limonite) and carbonatized. Several varieties occur. Mr. Floor [11] has found an amphibole of actinolitic to tremolitic composition with the following observed properties: $c/n_z = 21–24°$; birefringence = 0.004–0.006; $-2V = 68°$; color (megascopically) = very pale blue; structure = fibrous. An X-ray powder photograph points to an amphibole of actinolitic to tremolitic composition.

Also several hornblendes were found in thin sections and concentrates with pleochroic colors as follows—z = violet, ink blue, light green, bluish green etc., x = greenish blue, colorless to yellow, apple green etc., negative elongations, rather low to very low birefringences. Since the observed crystals were small or altered it was impossible to obtain more conclusive properties. The poor stated properties point to a soda-hornblende variety.

Very rarely there is found an amphibole with a positive elongation, a pleochroism from emerald green (z) to light green (x) and a rather low birefringence.

Zircon. This mineral mostly occurs as very small grains. In places crystals up to 6 mm were found. In one polished section a zircon was observed, which has replaced pyrochlore to a very small extent. The mineral itself was partly replaced by carbonates. In ultra-violet short wave illumination the mineral shows nearly always a bright yellow fluorescence.

[10] Laboratorium onderzoek van een carbonatietgesteente uit het voorkomen Panda Hill in Tanganyika, Leiden, Maart 1955.
[11] Student-geologist, State University, Leyden.

Olivine.—Olivine has been found in several dike rocks in the carbonatite. Commonly it is totally replaced by calcite and/or altered to serpentine. Pseudomorphs of calcite after olivine are conspicuous in thin sections. Alterations of a dark green color are probably garnierite. Reaction of olivine with the carbonatic country rock is apparent as most of the crystals show reaction rims.

Pyroxene.—In a drill-core sample an orthoclase-pyroxene rock was found. This pyroxene has a clinoestenitic composition.

Anatase.—Euhedral crystals were found in a strongly weathered meroxene-rich fenitic rock. X-ray powder diagrams point to anatase. These crystals (leucoxenic aggregates) are probably pseudomorphs after rutile.

So far petrographic investigations could be made only on a limited scale. It is certain that more thorough observations of thin sections, polished sections, and other petrographic methods, would reveal more data on the petrographical composition of the Mbeya carbonatite. Although several typical rocks of the carbonatite-suite have been found, it is not possible at this stage to give further information.

GEOLOGICAL DEPARTMENT,
MBEYA EXPLORATION COMPANY LTD.,
MBEYA, TANGANYIKA,
September 30, 1957

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CONTRIBUTIONS TO THE MINERALOGY OF EGYPTIAN MANGANESE DEPOSITS

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ABSTRACT

Mineralogical investigations are carried out on manganese and iron minerals from the manganiferous deposits of Sinai and the Eastern Desert. These investigations show that pyrolusite and manganite are the most widely distributed and predominant among the manganese minerals; psilomelane and cryptomelane are less common, and ramsdellite is uncommon being present only in minute amounts. Furthermore, the iron minerals are more abundant in Sinai, and they are essentially represented by goethite and less hematite.

During the present mineralogical studies, new data are recorded for the properties of the manganese and iron minerals especially their microhardness and reflectivity.

INTRODUCTION

THE chief manganiferous deposits in Egypt are found in two main areas, the first is west central Sinai and the second is the southern Eastern Desert (Fig. 1).

In west central Sinai manganese-iron deposits occur as lenses and lenticular bands in Carboniferous dolomitic limestone-clay horizon, especially near its base. A few smaller manganese iron deposits are found in sandstone. This is the most important source of manganese and manganiferous iron ores in Egypt and the area has produced some 4,000,000 metric tons of ore from 1918–1957.

In the Eastern Desert scattered manganese deposits with subsidiary iron minerals fill fault fissures and fissures of late Miocene age are found. In

most of the localities the ore occurs with calcite gangue and minor quartz in Middle Miocene sedimentary series consisting of limegrit, conglomerate, clay and sandstones. The ore fills the fault zones and fissures or replaces favorable wall-rock, especially limegrit and conglomerate. However, at few localities it occurs in fault zones and fissures cutting Precambrian rocks, for example, at Wadi Diib the deposit is located in pink granite, and at Wadi Mialik it is found in amphibolite (4).

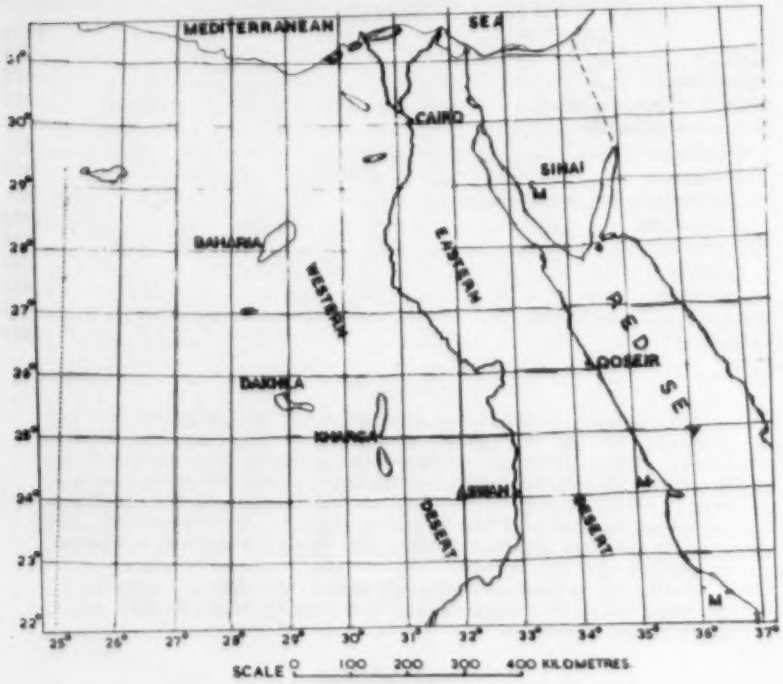

FIG. 1. Map of Egypt showing the position of the main manganiferous deposits (M) in Sinai and the Eastern Desert.

The purpose of the present work is to survey the mineralogical composition of the ores in the Eastern Desert and Sinai, and to examine the properties of the manganese-iron mineral association by various methods in order to aid in their future identification.

Minerals collected by the writers from the following localities in Sinai have been examined: Oleikat, Marahil, Um Sakran, Um Bogma, Um Sayalat, Wadi Nasib, Gebel Nasib and Higazia. Also the ores collected by E. M. El Shazly and F. A. Bassyuni from Wadi Mialik, Yoider, Wadi Diib, Eif

Onqwab, I Hubal, Gebel To Yu, Alafot, Matet Onqwab and Wadi Baloonay have been studied in the Eastern Desert.

A number of polished sections of the manganese and manganese iron ores from the above localities were examined under reflected light. Some of the specimens were selected for reflectivity measurements, micro-hardness tests and X-ray studies.

Previous mineralogical examinations of Egyptian manganese ores are not satisfactory and are contradictory as they depend mainly on identification in hand specimens. Ball (2) mentioned that the manganese and iron minerals in Sinai deposits are essentially composed of pyrolusite, psilomelane, wad and hematite. Fenine (5) added limonite to the previous minerals. Also Davey (3) reported the presence of manganite in Sinai, although his descriptions do not correspond to the properties of this mineral. Attia (1) mentioned that hausmannite, crednerite and hetaerolite are also found as minor constituents. Hollandite and coronadite are believed by Gill and Ford (7) to be present in the manganese iron deposits of Sinai.

METHODS OF INVESTIGATIONS

The specimens used in the present study were collected from their localities during geological examinations of the manganese and manganese iron deposits of Sinai and the Eastern Desert. More than two hundred polished and thin sections were examined. The polished sections were examined by an ore microscope for their optical properties, textures, and etch tests. About 20 specimens of the above were selected for examination by X-ray powder methods. Psilomelane and cryptomelane are in addition defined by analysis using a large quartz spectrograph to determine the intensities of the Ba and K lines. Also, reflectivity and micro-hardness measurements were carried out for the well defined minerals that are preferably coarse grained and not friable or powdery.

X-ray Powder Method.—Seifert & Co. apparatus was used, supplied by a current 10 M.A. and 30 K.V. The powdered sample was held on a glass fiber and photographed by 28 cm Ilford film in a Unicam powder camera of 9 cm diameter. Molybdenum radiation was used with manganese minerals and cobalt radiation was applied in the case of the iron minerals. The films produced were measured and correlated with the A.S.T.M. data and those presented by Ramdohr (9) for manganese minerals. The line intensities are expressed by the following symbols:

vs	very strong	w	weak
s	strong	vw	very weak
m	medium		

Reflectivity Measurements.—The method used for measuring reflectivity is similar to that suggested by Folinsbee (6). Reflectivity for selected specimens of minerals is measured using a Weston Master II universal exposure meter, which is fitted in the position of the ocular of a Reichert universal microscope Me F. Minerals are observed under the microscope using epilens

45 : 1. The source of light is a mercury vapor lamp "Mercurius" using red cut-off filter (R) and (R) and green (G) filters. Measurements were taken with standard well polished pyrite for comparison. The areas selected for measuring are free from inclusions especially in the field of view. The readings taken in candle foot lights are transformed into percentage of reflectivity for all the specimens examined both in (R) filter and (R) and G

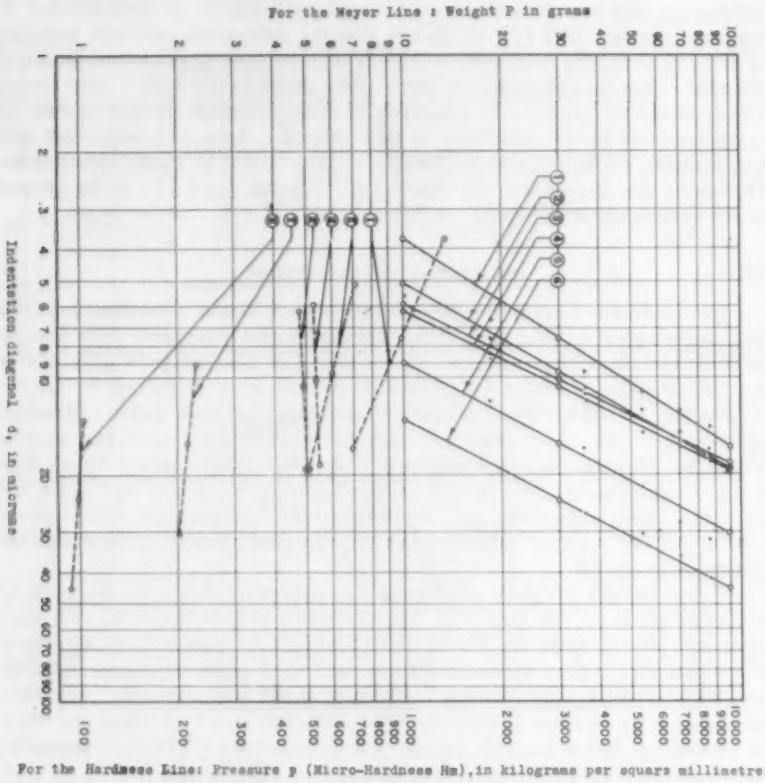
For the Meyer Line : Weight P in grams
Indentation diagonal d, in micron
For the Hardness Line: Pressure p (Micro-Hardness Hm),in kilograms per square millimetre.

FIG. 2. Measuring chart showing Meyer Lines and Hardness Lines of pyrolusite, goethite, manganite, psilomelane and ramsdellite

filters. Values of reflectivity were determined and tabled taking the reflection percentage of pyrite as 54.5 percent using (R) filter.

Micro-hardness.—Measurements of micro-hardness were carried out for a typical specimen of each of the minerals pyrolusite, psilomelane, ramsdellite and goethite as well as two specimens of manganite. For this purpose, Reichert micro-hardness tester no. 2760 was used in conjunction with Reichert

universal camera microscope, Me F. In this procedure Vickers micro-hardness is determined by producing an indentation in the mineral surface and measuring the diagonal of the indentation by optical means. The procedure is described in detail in a brochure issued by C. Reichert Optische Werke in 1950. Following this procedure the "Meyer line" and "Hardness line" for the specimens examined are shown in Figure 2.

Meyer Lines	Hardness Lines
(1) Pyrolusite	(I) Pyrolusite
(2) Goethite	(II) Goethite
(3) Manganite (dark variety)	(III) Manganite (dark variety)
(4) Manganite (normal variety)	(IV) Manganite (normal variety)
(5) Psilomelane	(V) Psilomelane
(6) Ramsdellite	(VI) Ramsdellite

MANGANESE MINERALS

Pyrolusite

Occurrence.—Pyrolusite was observed in all the localities examined in Sinai and the Eastern Desert where it is the most common manganese mineral.

Optical Properties.—The mineral occurs in coarse or medium prismatic crystals, or may form very fine grained aggregates. Banded texture with psilomelane is observed in Diib, Eastern Desert. Pyrolusite replaces other manganese minerals including manganite, psilomelane and ramsdellite. Veinlets of pyrolusite may also cut through goethite (Fig. 3). Under reflected light the mineral is white with a distinct yellow tint. Reflection pleochroism is clear and anisotropism is very strong except in very fine-grained aggregates. Pyrolusite may show traverse cracks perpendicular to the elongation of its crystals, this character is well exhibited by specimens from localities in the Eastern Desert (Fig. 4).

Reflectivity Measurements.—Pyrolusite gives the highest reflectivity values for all manganese and iron minerals examined. Reflectivity measurements were taken for four samples, and the results using R filter and R and G filters are given in Table 1. The average value for pyrolusite using R filter is 33.9 compared to the value of 54.5 given by pyrite. It may be noted that the values of pyrolusite range between 32.5 and 36.1. The two extreme values given by Folinsbee (6) for pyrolusite and "polianite" are 33.1 and 39.7 respectively, which are near those obtained by the writers.

Micro-hardness Measurements.—The measurements for a specimen of good crystalline pyrolusite from Gebel To Yu are given in Table 2, and the

TABLE 1

REFLECTIVITY VALUES FOR PYROLUSITE

Locality		Reflectivity values R filter	R and G filters
Wadi Diib	(Eastern Desert)	36.1	6.8
Hubal	(Eastern Desert)	33.5	6.4
Hegazia	(Sinai)	33.5	6.4
Gebel To Yu	(Eastern Desert)	32.5	6.0
Average		33.9	6.4

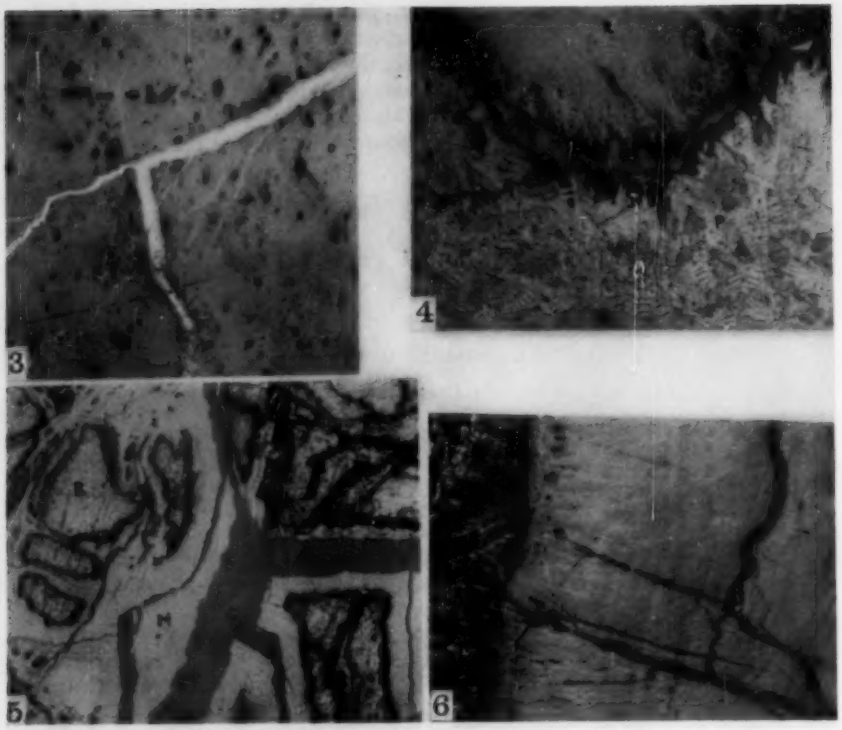

FIG. 3. Late pyrolusite veinlets cutting goethite, Um Sayalat (Sinai). Reflected light × 55.

FIG. 4. Ramsdellite (R) surrounded by a rim of dark manganite (M). Pyrolusite (P) showing traversal cracks is the main mineral present and occupies the outer peripheries of the other minerals, Gebel To Yu (Eastern Desert). Reflected light × 55.

FIG. 5. Ramsdellite (R) forming small cores in manganite (M), showing variations in brightness. Calcite veinlets (C) are observed cutting the manganite. Later veinlets of pyrolusite (P) cut all the minerals present in the section, Yoider (Eastern Desert). Reflected light × 22.

FIG. 6. Goethite with banded structure forming the outer rim of pyrolusite-manganite lens, Marahil (Sinai). Reflected light × 55.

Meyer and Hardness lines are plotted in Fig. 2. The available data indicates that pyrolusite is the hardest of all manganese and iron minerals examined. Moreover, the Hardness line slopes from the lower right to the top left in a notable manner, thus showing that smaller weights give greater hardnesses.

X-ray Diffraction Data.—Four samples from the following three localities are examined by the powder method, Oleikat and Marahil (Sinai) and Hubal (Eastern Desert). The data for the sample from Hubal are given in Table 3.

TABLE 2

MICRO-HARDNESS MEASUREMENTS FOR PYROLUSITE FROM GEBEL TO YU (EASTERN DESERT)

Dw	P	q	d
5	10	22	3.70
10	18.5	39	6.55
20	36	57	9.58
30	54	66	11.09
40	70	75	12.60
50	87	84	14.11

Hm (P 10, d 3.70) = 1353
Hm (P 30, d 7.50) = 988
Hm (P 100, d 16.30) = 697

TABLE 3

X-RAY DIFFRACTION DATA FOR PYROLUSITE FROM HUBAL (EASTERN DESERT)

d (Å)	Intensity
3.41	s
3.06	vs
2.40	s
2.19	vw
2.11	w
1.62	s
1.56	m

Manganite

Occurrence.—The mineral is found in all the localities investigated in the Eastern Desert and Sinai, where it is next to pyrolusite in abundance.

Optical Properties.—Two main varieties of manganite were distinguished according to their optical properties. The normal variety is present in both Sinai and the Eastern Desert, being especially well developed in the former. The normal manganite is generally in coarse to medium crystals with a mosaic texture, although it may be also fine grained. Under reflected light the color

TABLE 4

REFLECTIVITY VALUES FOR MANGANITE

Variety	Locality		Reflectivity values	
			R filter	R & G filters
Normal	Hubal	(Eastern Desert)	26.8	4.7
	Eif Onqwab	(Eastern Desert)	26.8	4.7
	Wadi Nasib	(Sinai)	25.7	4.3
	Oleikat	(Sinai)	25.7	4.3
	Hegazia	(Sinai)	24.5	4.2
	Wadi Diib	(Eastern Desert)	24.5	4.2
	Average		25.7	4.4
Dark	Gebel To Yu	(Eastern Desert)	21.0	3.8
	Yoider	(Eastern Desert)	21.0	3.8

is grayish white to brownish gray. Reflection pleochroism is weak, from light grayish brown to dark gray with brownish tint. Strong anisotropism, red internal reflection and twinning are exhibited by this variety in the same manner as described by Uytenbogaardt (12).

The second variety of manganite is found only in the Eastern Desert. It is very fine grained and possesses a darker gray color with a brownish tint. Anisotropism is weaker compared to the normal variety, while internal reflection is not clear.

Reflectivity Measurements.—The reflectivity values for manganite are the lowest for all manganese minerals examined. The average reflectivity value for the normal variety of manganite is 25.7 using R filter which is slightly lower than that of ramsdellite, but much lower than for psilomelane and pyrolusite. The reflectivity value for the darker variety of manganite is 21.0 using R filter, being considerably lower than the normal variety, but equal to the value given by goethite (Table 12).

TABLE 5

MICRO-HARDNESS MEASUREMENTS FOR MANGANITE

1. Normal variety from Oleikat (Sinai)

Dw	P	q	d
5	10	33	5.54
10	18.5	50	8.40
20	36	70	11.76
30	54	88	14.78
40	70	97	16.30
50	87	107	17.98

Hm (P 10, d 6.2) = 482
Hm (P 30, d 10.6) = 494
Hm (P 100, d 19.2) = 503

2. Darker variety from Yoider (Eastern Desert)

Dw	P	q	d
5	10	35	5.88
10	18.5	52	8.74
20	36	67	11.26
30	54	80	13.44
40	70	92	15.46
50	87	100	16.80

Hm (P 10, d 5.9) = 532
Hm (P 30, d 10.15) = 540
Hm (P 100, d 18.4) = 547

Micro-hardness.—Two specimens were tested by this method, the first belonging to the normal variety from Oleikat, and the second to the darker variety from Yoider. The available data suggests that manganite is next in hardness to pyrolusite among the manganese minerals examined. The normal variety of manganite, however, is slightly softer than the darker variety. Moreover, the Meyer lines (Fig. 2) show that the normal variety of manganite is softer than goethite, while the darker variety is softer than goethite only for loads smaller than 60 grams. The relation between the microhardness of goethite to that of normal manganite agrees with the Vicker's

hardness values given by Nakhla (8) who demonstrated that manganite is softer than goethite. The Talmage hardness for manganite and goethite (from Short, 11) is different, as manganite (E^+) is considered harder than goethite (E), although both belong to the same class. The Hardness lines in the case of manganite are parallel for both varieties and sloping gently from the lower left to top right (Fig. 2), indicating that the smaller weights applied correspond to smaller hardnesses. It may be noted that manganite is the only mineral examined exhibiting this feature.

X-ray Diffraction Data.—A specimen of normal manganite from Oleikat was examined using X-ray powder method, the data obtained is given in Table 6. Attempts to take clear films for the powder of the dark variety failed.

Psilomelane and Cryptomelane

Occurrence.—Both minerals are widely distributed in most of the localities examined. They are fairly abundant especially in Sinai. In general they are next in abundance to pyrolusite and manganite.

TABLE 6

X-RAY DIFFRACTION DATA FOR NORMAL MANGANITE FROM OLEIKAT (SINAI)

d (Å)	Intensity
3.42	s
2.69	m
2.42	m
2.10	w
1.80	m
1.62	m
1.52	s
1.44	m
1.29	w
1.11	m

Optical Properties.—Psilomelane and cryptomelane are either colloform (Eastern Desert), massive (Sinai) or in fine aggregates of acicular crystals. Shrinkage cracks are common. In Diib locality in the Eastern Desert a rhythmic texture is exhibited in alternation with fine pyrolusite. Optical properties are similar to those mentioned by Uytenbogaardt (12). The most prominent include color, which is bluish gray to grayish white under reflected light; reflection pleochroism is generally from bluish white to dull bluish gray; anisotropism is notable from white to gray colors and extinction is straight.

Distinction between psilomelane and cryptomelane by optical properties is not definite, as both are very similar.

Spectrographic Analysis.—For distinction between psilomelane and cryptomelane spectrographic analysis is a useful method. The intensity of the Ba line 4554.0 Å and the K line 4047.2 Å gives an idea whether the mineral is psilomelane or cryptomelane. Psilomelane shows strong Ba lines and faint K lines, while cryptomelane shows strong K lines and weak Ba lines. In some cases K and Ba lines are strong indicating the intimate association of the two minerals.

TABLE 7

REFLECTIVITY VALUES FOR PSILOMELANE AND CRYPTOMELANE

Locality			Reflectivity values R filter	Reflectivity values R and G filters
Cryptomelane	Oleikat	(Sinai)	31.5	6.0
Psilomelane	Oleikat	(Sinai)	31.5	6.0
Psilomelane	Marahil	(Sinai)	31.5	6.0
Psilomelane	Wadi Diib	(Eastern Desert)	31.5	6.0
Average			31.5	6.0

Reflectivity Measurements.—The values for four specimens are constant being 31.5 using R filter compared to the value of 54.5 given by pyrite. Reflectivity values given by Folinsbee (12) are 28.3–32.7 for psilomelane, no value is given for cryptomelane. The readings for psilomelane and cryptomelane are the same in the present study. They are slightly lower than pyrolusite and considerably higher than the other manganese and iron minerals examined.

Micro-hardness Measurements.—The measurements for a specimen of massive psilomelane from Oleikat are given in Table 8. It is shown on the

TABLE 8

MICRO-HARDNESS MEASUREMENTS FOR PSILOMELANE FROM OLEIKAT (SINAI)

Dw	P	q	d
5	10	53	8.90
10	18.5	70	11.76
20	36	98	16.46
30	54	130	21.84
40	70	166	27.89
50	87	186	31.25

Hm (P 10, d 8.95) = 231
Hm (P 30, d 16.00) = 217
Hm (P 100, d 30.20) = 203

measuring chart (Fig. 2) that psilomelane is softer than pyrolusite, goethite and manganite but considerably harder than ramsdellite. The Hardness line of psilomelane slopes gently from the top left to the lower right in the measuring chart, indicating that smaller weights applied give greater hardnesses.

X-ray Diffraction Data.—Four specimens of psilomelane from Wadi Diib Oleikat and Marahil, and one specimen of cryptomelane from Oleikat, are examined by the powder method. Table 9 gives the lines and intensities obtained for the specimen of psilomelane from Marahil.

TABLE 9

X-RAY DIFFRACTION DATA FOR PSILOMELANE FROM MARAHIL (SINAI)

d (Å)	Intensity
3.25	s
2.43	vs
2.18	m
1.85	m
1.56	m
1.36	w

Ramsdellite

Occurrence.—Ramsdellite is found in minute quantities. It is more common in the deposits of the Eastern Desert as compared to Sinai. The mineral occurs at Yoider and Gebel To Yu in the Eastern Desert and at Um Bogma in Sinai.

Optical Properties.—Ramsdellite is found in small patches of fine grained fibrous and easily cleavable crystals, enclosed by manganite, pyrolusite or both (Figs. 4, 5). It is easily replaced by pyrolusite. The color of ramsdellite is iron black in handspecimen, but yellowish white under the ore microscope. Its reflection pleochroism is clear, but more so in oil. Internal reflection is clear in oil, being deep purple at the margin. The mineral is weakly anisotropic, and on the whole the optical properties observed by the writers are similar to those noted by Ramdohr (9).

TABLE 10

REFLECTIVITY VALUES FOR RAMSDELLITE

Locality	Reflectivity values R filter	R and G filters
Yoider (Eastern Desert)	26.8	4.7
Gebel To Yu (Eastern Desert)	25.6	4.3
Average	26.2	4.5

Reflectivity Measurements.—The values of reflectivity listed in Table 10 show that ramsdellite is distinctly lower than pyrolusite and psilomelane, and slightly higher than the normal variety of manganite. The average value for ramsdellite from the Eastern Desert using R filter is 26.2 compared to pyrite 54.5.

TABLE 11

MICRO-HARDNESS MEASUREMENTS OF RAMSDELLITE FROM YOIDER (EASTERN DESERT)

Dw	P	q	d
5	10	80	13.44
10	18.5	120	20.16
20	36	155	26.04
30	54	180	30.24
40	70	210	35.28
50	87	245	41.16

Hm (P 10, d 13.4) = 103
Hm (P 30, d 23.7) = 99
Hm (P 100, d 44.5) = 93

Micro-hardness Measurements.—The measurements for a ramsdellite specimen from Yoider are given in Table 11, while the Meyer and Hardness lines are plotted in Figure 2. It is clear from the data of micro-hardness that ramsdellite is by far the softest of all the manganese and iron minerals examined. This fact is also very obvious by the marked relief between ramsdellite and pyrolusite and manganite produced by polishing. The Hardness

TABLE 12

REFLECTIVITY VALUES FOR GOETHITE

Locality	Reflectivity values *R* filter	*R* and G filters
Um Sayalat (Sinai)	21.0	3.8
Marahil (Sinai)	21.0	3.8
Marahil (Sinai)	21.0	3.8
Average	21.0	3.8

line runs with a gentle slope from the lower right to the top left as shown in Figure 2.

X-ray Diffraction Data.—The X-ray powder photographs of minute samples of ramsdellite taken by a small drill are not clear.

IRON MINERALS

Goethite

Occurrence.—Although present in all the localities examined in Sinai and the Eastern Desert, however, it is far more abundant in the former. In some places goethite forms the outer zone of the manganese iron orebodies, but it may be also distributed in various parts.

Optical Properties.—Radiating botroiydal crystalline masses with banded structure are noted in Sinai (Fig. 6), while in the Eastern Desert goethite is cryptocrystalline and massive. Color under reflected light is light to dark gray with a bluish tint, cryptocrystalline goethite from the Eastern Desert is dark gray. The reflection pleochroism and anisotropism are in agreement with those mentioned by Uytenbogaardt (12). Internal reflection is brownish yellow or reddish brown, and it is especially notable in microcrystalline goethite from the Eastern Desert.

Reflectivity Measurements.—Goethite and the dark variety of manganite give the lowest reflectivity values of all minerals examined. Reflectivity measurements were taken for three good crystalline specimens from Sinai, and the results are listed in Tabie 12. The value given (21 using R filter) is higher than that obtained by Folinsbee (6) which is 16.1.

Micro-hardness Measurements.—Data for a specimen of good crystalline goethite from Marahil indicates that goethite comes next in hardness to

TABLE 13

MICRO-HARDNESS MEASUREMENTS FOR GOETHITE FROM MARAHIL (SINAI)

Dw	P	q	d
5	10	30	5.04
10	18.5	45	7.56
20	36	64	16.75
30	54	75	12.60
40	70	88	14.78
50	87	105	17.44

Hm (P 10, d 5.10) = 713
Hm (P 30, d 9.60) = 604
Hm (P 100, d 19.00) = 513

pyrolusite. Goethite is harder than the normal variety of manganite. It is also harder than the dark variety of manganite for loads from 10–60 grams and softer for loads ranging from 60–100 grams. The Hardness line for goethite (Fig. 2) slopes moderately from the top left to the lower right of the measuring chart.

X-ray Diffraction Data.—Several specimens of microcrystalline goethite from Alafot in the Eastern Desert and coarse goethite from Marahil and other localities in west central Sinai were examined by the powder method. The list of lines and their intensities for the mineral from Marahil are given in Table 14.

Hematite

Occurrence.—The mineral is common in Sinai, but evidently less abundant than goethite.

Optical Properties.—The hematite present is generally cryptocrystalline. In handspecimen it is blood red to brownish red in color. Optical properties

TABLE 14

X-RAY DIFFRACTION DATA FOR GOETHITE FROM MARAHIL (SINAI)

d (Å)	Intensity	d (Å)	Intensity	d (Å)	Intensity
5.10	w	1.72	s	1.29	vw
4.24	vs	1.70	w	1.27	vw
3.41	w	1.67	vw	1.24	vw
2.72	vs	1.61	w	1.20	w
2.62	w-m	1.57	m	1.14	vw
2.47	vs	1.51	m	1.13	w
2.28	m	1.46	m	1.07	vw
2.22	m	1.42	w	1.05	vw
2.03	vw	1.40	w	1.02	w
1.93	w	1.37	w	1.01	w
1.82	m	1.32	m	1.00	w

are not clear because of its presence in very small grains and due to its friability. Micro-hardness and reflectivity are not determined for the same reason. The mineral may be largely derived from goethite by dehydration.

X-ray Diffraction Data.—Several specimens of hematite from Marahil, Oleikat and other localities are examined using X-ray powder method. The data obtained for a specimen from Oleikat is given in Table 15.

SUMMARY AND CONCLUSIONS

1. The ore minerals in the manganiferous deposits in Sinai and the Eastern Desert show great similarity in spite of the differences in the geological mode of occurrence in the two regions. The manganese minerals are mainly represented by pyrolusite followed by manganite and less abundant psilomelane and cryptomelane. Ramsdellite is also present but it is not common, and when present it is found only in minute quantities. The iron oxides asso-

TABLE 15

X-RAY DIFFRACTION DATA FOR HEMATITE FROM OLEIKAT (SINAI)

d (Å)	Intensity	d (Å)	Intensity
3.71	m	1.45	s
2.72	vs	1.31	m
2.54	s	1.26	w-m
2.22	m	1.19	w
1.85	s	1.16	w
1.70	vs	1.14	m
1.60	w-m	1.10	m
1.49	s	1.05	m-s

ciated with the manganiferous ores are essentially represented by goethite. Hematite is less common being particularly noted in Sinai deposits. As a general rule the iron oxides are much more abundant in Sinai in comparison to the Eastern Desert.

2. The optical properties under reflected light of well polished specimens represent good criteria for the identification of most of the minerals examined. However, the X-ray powder method is necessary for the identification of powdery, friable and cryptocrystalline material.

3. The distinction between psilomelane and cryptomelane and their mixtures may be best achieved by spectrographic methods determining the intensities of Ba and K lines.

TABLE 16

REFLECTIVITY VALUES OF THE EXAMINED MINERALS

Mineral	No. of specimens examined	Maximum value	Minimum value	Average value
A. Using *R* filter				
Pyrite	1			54.5
Pyrolusite	4	36.1	32.5	33.9
Psilomelane	3			31.5
Cryptomelane	1			31.5
Ramsdellite	2	26.8	25.6	26.2
Manganite (normal)	6	26.8	24.5	25.7
Manganite (dark)	2			21.0
Goethite	3			21.0
B. Using *R* and G filters				
Pyrite	1			11.5
Pyrolusite	4	6.8	6.0	6.4
Psilomelane	3			6
Cryptomelane	1			6
Ramsdellite	2	4.7	4.3	4.5
Manganite (normal)	6	4.7	4.2	4.4
Manganite (dark)	2			3.8
Geothite	3			3.8

4. Measurements of reflectivity help in the identification of the examined minerals provided they are well polished and comparatively free from inclusions. The highest reflectivity is exhibited by pyrolusite, followed by psilomelane and cryptomelane. Ramsdellite and normal manganite show moderate reflectivity, and the lowest values are exhibited by goethite and the dark variety of manganite. The reflectivity values given by the examined minerals in comparison with pyrite, are listed in Table 16.

5. The minerals show a considerable degree of variation in their microhardness with the exception of goethite and manganite. The results of the investigations are plotted in Figure 2, where the minerals are arranged in the following order starting from the hardest and ending with the softest: pyrolusite, goethite, dark manganite, normal manganite, psilomelane and finally ramsdellite. No data are recorded for hematite as the available specimens are not suitable for examination by this method. The dark manganite is softer than goethite for weights less than 60 grams, and harder under loads greater than 60 grams. The Hardness lines slope in all the minerals examined from the lower right to the top left, indicating that smaller weights give greater hardnesses in such cases. With manganite the hardness lines in both varieties slope from the top right to the lower left, thus showing that smaller weights correspond to smaller hardnesses.

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MINERAL RESEARCH LABORATORIES,
DOKKI, CAIRO,
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FORMATION OF SULFUR BY REDUCTION OF ANHYDRITE AT RAS GEMSA, EGYPT

G. A. SCHNELLMANN

ABSTRACT

Reduction of dissolved sulfates by bacteria to produce elemental sulfur at ordinary temperatures is an established process, but Hofman and Mostowitsch's work has been generally held to prove that reduction in the solid state by inorganic processes cannot take place below 800° C. The Ras Gemsa sulfur deposit affords new field evidence that conflicts with these laboratory data, and it is concluded that inorganic reduction can, in fact, occur at moderate temperatures. This view is supported by Gualtieri's interpretation of the origin of the Italian sulfur deposits. It is suggested that the laboratory and field evidence can be reconciled by appeal to the effect of an unidentified catalyst.

INTRODUCTION

It is understood that a verbal communication on the sulfur deposit at Ras Gemsa, Egypt, was made to a Symposium on Applied Geology in the Near East held at Ankara in 1955, but so far as can be ascertained there is no published account. Although the deposit is small by world standards, it is of importance to Egypt's economy, and certain of its features appear to the writer (who made a professional examination of it in December 1957) to merit record as presenting field geological data on the natural reduction of sulfates that are at variance with currently accepted views based on chemical laboratory research.

Locations.—Ras Gemsa is a small peninsula on the western side of the Gulf of Suez, approximately 300 km south of the port of Suez and 100 km south of the producing oil field and port of Ras Gharib (Fig. 1). It is itself the site of an oil-field now almost exhausted. The two sides of the peninsula consist of high ground known, respectively, as the Western and Eastern Heights, the intervening tract of low ground being known as Happy Valley. Separated by a lagoon to the west of Ras Gemsa is Little Gemsa which affords evidence on the general geological structure but is not known to contain any sulfur deposits.

History.—It is not known when the sulfur was discovered, but the first attempt to work it was made by a French company in 1883. This failed following litigation, and no further work was undertaken until 1935, when there was an attempt to establish a superphosphate industry based on the Safaga phosphate deposits and sulfuric acid to be produced from the Ras Gemsa sulfur. Production costs proved uneconomic however, and this operation was short-lived. No further work was undertaken until the present operators, Société Egyptienne d'Engrais et d'Industries Chimiques S.A.E.,

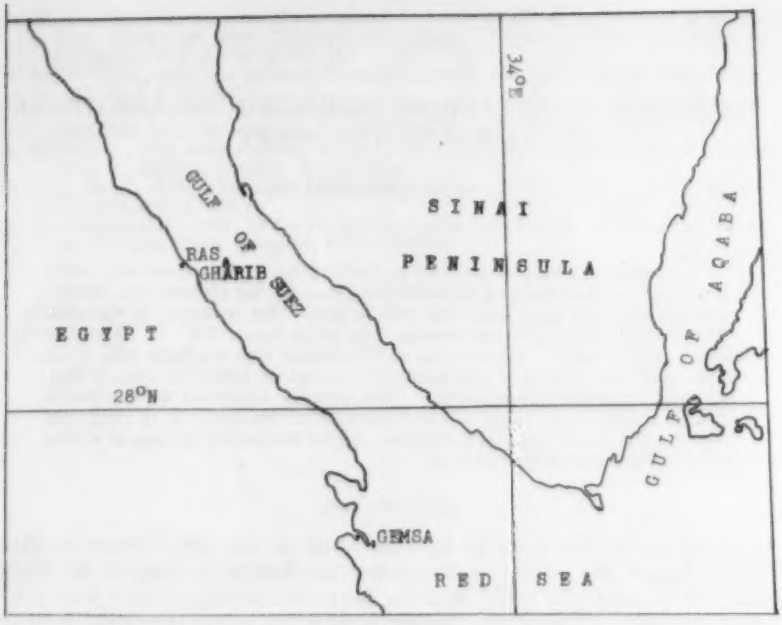

FIG. 1.

acquired the mining rights in 1953. Since that time development work has been in progress with a view to establishing sufficient reserves to justify the installation of a concentrating plant, a flow-sheet based on flotation using sea-water having meanwhile been worked out. During the period of inactivity oil was discovered beneath the peninsula. This is now approaching exhaustion, but the boreholes sunk during this phase provide significant data on the sulfur occurrence.

STRATIGRAPHY AND STRUCTURE

The Ras Gemsa peninsula consists of sediments of Miocene age comprising anhydrite and dolomite beds with interbedded marls. A few aragonite layers also occur in an environment which suggests as will be shown later, that they are not original sediments but have been formed by the reduction of anhydrite. Oil-well logs prove that evaporites continue in depth. Analyses show that the dolomite is anhydritic, containing up to 23 percent calcium sulfate, and that the anhydrite beds may contain up to 50 percent silica, which is attributed by Shukri (4) to diatomaceous bands. The beds dip to the north-east at about 15 degrees, and as a result of this a true thickness of approximately 240 m of strata is exposed. The western heights consist

almost entirely of anhydrite, the individual beds (which vary from 2 to 11 m in thickness and are most commonly 3–4 m) being separated by light gray to greenish marls generally about ½ m thick. Sixteen marl bands can be seen in the western cliffs, the highest of them differing from the others in being 5 m thick and variegated dark green and red in color. Because of the lithological monotony of the succession, correlation is difficult unless exposures can be traced continuously, but what appears to be an exposure of the same thick variegated marl farther east is most probably a similar bed 28 m (stratigraphically) higher. This upper variegated marl is overlain by 10 m of anhydrite, above which is a dolomite bed dipping into Happy Valley. Boreholes and pits show the valley to be occupied by anhydrite, whereas the eastern heights consist almost entirely of dolomite.

The clue to the structure is provided by Little Gemsa, where the beds dip to the south-west, thus establishing that Ras Gemsa is on the flank of an anticline, the crest of which has been eroded and is occupied by the lagoon. A strike fault of indeterminate throw marks the north-east side of Happy Valley and it is possible that other strike faults occur, although this cannot be established with certainty in the absence of diagnostic marker beds. Fissures in the strike direction are certainly common and may have affected the location of the sulfur, but there is no evidence of dip-faulting.

MINERALIZATION

The mineralization consists of elemental sulfur, locally and in places extensively contaminated by hydrocarbons. There are three main types of ore:

(1) Anhydritic: A fine dissemination of sulfur in anhydrite.
(2) Aragonitic: A coarser deposition of crystalline sulfur in the spaces between rosettes of crystalline aragonite.
(3) Dolomitic: Coarse crystalline sulfur lining the walls of fissures and cavities in the dolomite, but not penetrating to any great extent into the main mass of the rock.

In addition to these, which are regarded as primary types, there is one spectacular occurrence of botryoidal sulfur encrusting the walls of a large cavern. This is thought to be of secondary origin, since the normally sulfur-bearing aragonite is barren in the vicinity.

The various sulfur-bearing horizons invariably occur immediately below a marl bed, an environment at once calling to mind the well-established trapping or impounding mechanism.

ORIGIN

There is a not unnatural tendency to assume that the sulfur was derived from volatile sulfur compounds seeping upwards from the underlying oil (which is in fact of sulfurous type), but this facile explanation does not account satisfactorily for certain of the features. Partial oxidation of hy-

drogen sulfide, for example, which has been demonstrated to be an effective mechanism for sulfur deposits with volcanic associations, cannot be accepted in this case since the oil-wells prove the sulfur to continue well below the zone of aeration. On the other hand bacterial action, which is not dependent on oxidizing conditions and has long been known to be capable of producing sulfur by the reduction of sulfates in solution (1) is most unlikely to have been restricted to the impounding environment, even if it can take place in the solid. Since the origin now proposed devolves on the aragonitic ore, however, the remainder of this paper deals with this to the exclusion of other types.

In the first instance, the aragonite—calcium carbonate—occupies an anomalous stratigraphical position. The succession points to periods of desiccation (represented by the anhydrite) alternating with marine incursions (represented by the marl bands) which took place before the chloride stage of the evaporite series had been reached. Now it has long been established experimentally that the evaporite series begins with calcium carbonate (which is deposited when the volume of the sea water has been reduced to 50 percent, anyhydrite not being precipitated until the volume is 20 percent of the original), and this conforms with field observation of evaporites. Unless one makes some highly improbable postulates concerning the composition of the particular sea that gave rise to the Ras Gemsa evaporites, it is impossible that each cycle should be, as at first glance it appears to be, an inversion of the standard sequence.

Further suspicion as to the origin of the aragonite is aroused by its common eucrystalline habit; the aragonite layer generally consists of radiating groups of coarsely acicular crystals. Interference of the various stellate groups with each other has left cavities in which the sulfur, also commonly eucrystalline, occurs. This cavitation, it is submitted, is symptomatic of origin by formation from anhydrite, since the molecular volume of aragonite is approximately 25 percent less than that of anhydrite, and the postulated reaction is equimolecular, viz.,

$$n \cdot CaSO_4 + C_nH_{2n+2} = n \cdot CaCO_3 + n \cdot S + n \cdot H_2O + H_2.$$

A third phenomenon calling for explanation is the morphological relationship between the aragonite and the underlying anhydrite. They are not separated by the bedding plane that typically separates sediments (as, for example, the subface and superface of the various marl bands), nor is there a gradual transition such as would be expected when one solute starts to precipitate before the complete deposition of an earlier precipitated solute. The anhydrite/aragonite interface is sharply defined, but markedly undulatory. Any suggestion that this represents a sub-aerial denudation surface can be immediately ruled out by the impossibility that the invading sea would start to precipitate its dissolved matter (represented by the aragonite) before it had deposited its mechanically suspended matter (represented by the argillaceous content of the marls). This surface appears to the writer rather to

represent a "front" of chemical reaction between pre-existing anhydrite and hydrocarbon volatiles trapped beneath the impermeable marl.

This view finds support in Gualtieri's (2) researches on the origin of the Sicilian sulfur deposits, which he ascribes to the transformation of gypsum into calcite and sulfur, making the following points that conform with the field evidence of the aragonitic ore at Ras Gemsa: (i) the transformation tended to proceed along the strata; (ii) in the transformation from gypsum to sulfur-ore, there is a reduction in volume; (iii) sterile carbonate is the result of migration of the sulfur from the place in which the gypsum was reduced.

It is realized that this conception is in conflict with the generally held view that reduction of gypsum cannot be effected by inorganic processes below 700° C. This is based on the paper by Hoffman and Mostowitsch (3), a study of which reveals that it is not in fact relevant, since the experiments described do not result in the formation of elemental sulfur. They are concerned with the reduction of calcium sulfate by carbon or carbon monoxide to produce calcium sulfide, and with the oxidation of the calcium sulfide so formed. There is no suggestion of the separation of elemental sulfur, although the following two side reactions result in the removal of sulfur as volatile compounds:

$$CaS + 2H_2O \rightarrow Ca(OH)_2 + H_2S$$
$$CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2.$$

Neither of these are relevant since the second only occurs in the temperature range 800 to 900° C, and although the first takes place at ordinary room temperatures, it entails the prior formation of calcium sulfide at high temperatures. Nothing in the Ras Gemsa deposits and associated rocks suggests that they have been subjected to high temperatures. Hofman and Mostowitsch were at some pains to ensure the purity of their reagents, and it is not impossible that under less rigid conditions—natural as opposed to laboratory—some extraneous material may have had a catalytic effect that resulted in the reactions proceeding at much lower temperatures. Perhaps even more probably, on the field evidence, the Hofman and Mostowitsch reactions should be completely ignored. The hydrocarbons are obvious potential reducing agents, and though this does not solve the problem in the absence of appropriate chemical research, the field evidence points inescapably, in the writer's submission, to the formation of the sulfur by reduction of calcium sulfates at moderate temperatures and by inorganic processes.

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PYRITE INVESTIGATIONS AT NAIRNE, SOUTH AUSTRALIA

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ABSTRACT

The sulfide deposit, which is the Nairne Pyritic Formation, contains at least five varieties of FeS_2, three of which are of secondary origin. The main bulk of the FeS_2 is pyrite that probably owes its origin to sedimentary and subsequent metamorphic processes. Some of the FeS_2 occurs as pyrite in relatively large veins containing a suite of Ag-Sb minerals; these veins may have a hydrothermal origin.

Two varieties of secondary FeS_2 are the result of pyrrhotite alteration. The concentric FeS_2 consists of pyrite, marcasite, or pyrite and marcasite. It is characterized by a porous concentric structure and is extremely fine grained, thus presenting problems in flotation. The zoned pyrite may be either a direct replacement of the pyrrhotite or a replacement of the concentric FeS_2. The third variety of secondary FeS_2 occurs with zeolite, siderite, and limonite and is definitely a product of weathering.

INTRODUCTION

In September, 1957, the author became interested in the sulfide mineralization at Nairne, South Australia, because of the poor recovery of pyrite in flotation during that period. The following analysis of flotation concentrate and tailing from Grassfire Hill ore clearly demonstrates that concentric pyrite is the non-floatable pyrite, and that it significantly affects the pyrite recovery:

	Flotation concentrate	Flotation tailing
% wt. superpanner con.	48	7
% vol. clear pyrite	85	16
% vol. concentric pyrite	13	74
% vol. pyrrhotite	2	trace
% vol. sphalerite	trace	trace
% vol. chalcopyrite	trace	—
% vol. limonite etc.	trace	10

Because of the economic significance of the concentric pyrite, an investigation was initiated to ascertain the nature of this material, and the depth to which it persists. A study of surface and bore core samples disclosed that there are probably five types of FeS_2 at Nairne, three of which are of secondary origin.

This investigation was made possible by the U. S. Educational Foundation in Australia, the South Australia Department of Mines, and by the willing co-operation of Mr. J. Hammer, Mine Manager at Nairne.

GENERAL GEOLOGY AND MINERALOGY

The pyrite deposits at Nairne are part of the Nairne Pyritic Formation which is a member of the Kanmantoo Group, consisting of 26,000 feet of fine-grained quartzites, siltstones, and graywackes. The Nairne Pyritic Formation (believed to be Cambro-Ordovician in age) has been traced for over 65 miles, and locally at Nairne it thickens, and the beds dip approximately 70° E and strike generally N-S.

The deposit consists essentially of pyrite and pyrrhotite, with pyrrhotite being somewhat more predominant than pyrite; the deposit is worked by open cut mining for its sulfur content. Small amounts of galena, sphalerite, chalcopyrite, rutile, and arsenopyrite also occur. The sulfides are present as small grains distributed parallel with the bedding, and at Nairne are concentrated into economic proportions in three beds. These beds are 50 to 100 feet thick and are separated by waste beds, approximately 20 feet thick. Small veinlets of pyrite and pyrrhotite cut the bedding; these are believed to have been developed during metamorphism. Larger veins are also present and these commonly contain not only pyrite and pyrrhotite but also an assemblage of Ag-Sb minerals; these veins may be hydrothermal in origin.

Surface weathering has affected the deposit and has produced a gossan capping that is 60 feet thick in places.

A shear zone occurs just to the north of the quarries and has fractured the ore to some extent.

VARIETIES OF FeS_2

Investigations show that there are at least five varieties of FeS_2 present, three of which are of secondary origin.

Primary Pyrite.—The term primary pyrite is used here to designate the variety that occurs as small (2 mm and less) grains distributed parallel with the bedding, and also that variety in small tension gashes. This pyrite is considered to be of sedimentary origin and its initial form was possibly as hydrous iron sulfides. The grains are idioblastic to subidioblastic. Pyrite in contact with pyrrhotite tends to exhibit good crystal outlines whereas pyrite in contact with gangue tends to exhibit irregular outlines.

Internally the pyrite is generally clear with no inclusions. Rarely one finds a few grains that contain a number of minute unoriented inclusions of pyrrhotite and sphalerite. Some of the pyrite grains are anisotropic and not isotropic as should be expected from a cubic mineral. Anisotropism, however, could come about by distortion of the crystal lattice, which could be

caused by foreign elements in the pyrite. Some particularly anisotropic grains were separated and analyzed. The analysis showed .2% Ni which might account for the anomalous anistropism.

This variety of pyrite accounts for approximately 90 percent of the pyrite in the formation. It is resistant to weathering and is commonly found unaltered even where the feldspar and pyrrhotite have been decomposed.

Vein Pyrite.—This term designates pyrite found in the larger veins along with the rare Ag-Sb minerals. It is coarser grained than the primary pyrite (grains up to 5 cm across) and is more commonly euhedral. Inclusions are encountered in some of the grains but they are by no means numerous. The pyrite is not uncommonly fractured and the fractures are filled with pyrrhotite, galena, and chalcopyrite. This variety of pyrite is rarely anisotropic.

Vein pyrite constitutes approximately 5 percent of the pyrite in the ore deposit. It is also resistant to alteration and is commonly enclosed by altered pyrrhotite.

A partial spectrographic analysis of these two varieties of pyrite (analyses by A. B. Timms, S. A. Department of Mines) shows:

	Fe	S	Ni	Co	Mn	Ti
P. P.	46.3	52.5	.01	.02	.07	.05
V. P.	47.5	53.0	.01	.06	.005	.01

Pyrite is a non-stoichiometric compound and according to Edwards (3) may vary in composition from $FeS_{1.94}$ to $FeS_{2.05}$. By recalculating the above Fe-S ratios to 100 percent it is evident that primary pyrite has a composition of $FeS_{1.98}$ whereas vein pyrite has a composition of $FeS_{1.94}$. The samples were pure as far as could be ascertained although a few impurities may have come in a inclusions. If the material is considered to be pure, however, then both pyrites do not have the same composition. Skinner (8) has demonstrated to his satisfaction that the pyrite has a constant composition regardless of the other minerals present. If so, one would expect the composition of both varieties of pyrite to be the same. Since they do not appear to be, it may be that the vein pyrite was formed after the formation of the main body of sulfides.

As regards the other elements, Co and Ni may enter into the pyrite lattice in substitution solid solution and may be responsible for the anomalous anisotropism observed in some of the pyrite grains.

Secondary FeS_2.—Three varieties of secondary iron sulfide are present; two of these are replacement products of pyrrhotite and the third represents deposition from circulating ground water. The first two represent approximately 5–10 percent of the pyrite in the ore deposit and are of definite economic significance; the third is a curiosity, representing less than .1 percent of the pyrite.

Replacement Products of Pyrrhotite

The replacement products of pyrrhotite are referred to here as concentric FeS_2 and zoned pyrite; they occur in roughly equal proportions.

Concentric FeS_2.—This type of FeS_2 is responsible for the poor recovery of pyrite, especially in Grassfire Hill ore. In the typical example pyrrhotite is partially replaced by little olive drab nodules as much as 5 mm in diameter; these tend to form masses suggestive of bunches of grapes. Under a binocular microscope these are found to consist of a number of concentric shells composed of extremely fine-grained material; electron photomicrographs disclose that the grains are commonly less than .5 microns in diameter, although 2 microns is more the rule. In a number of instances the grains of one shell are markedly coarser than those in the adjacent shell. The shells commonly appear to be separated in places by a thin (approximately 3 microns in thickness) void parallelling the outline of the shell. These voids account for the concentric cracks observed in polished section (Fig. 1). In some specimens the material is rather porous, displaying numerous randomly-spaced voids less than 3 microns in diameter. The porous nature of the material and the fine grain size are most probably the main factors hampering proper flotation. The voids probably absorb the reagents and the rough irregular surface probably makes bubble attachment difficult.

Under the reflecting microscope the picture becomes more complex. I find that some of the nodules consist exclusively of pyrite, others of marcasite, and others of a mixture of pyrite and marcasite. The marcasite is typically bluish white in color whereas the pyrite is brownish yellow, slightly darker than ordinary pyrite. In some of the nodules the marcasite is disseminated throughout the pyrite (or vice versa) and in others the pyrite and marcasite form alternating bands. In those nodules composed of marcasite, a broad pattern of anisotropism is commonly encountered. This pattern passes over the concentric cracks, tending to indicate that the cracks were produced after the initial material had been formed and the structure developed.

Structurally there are two main types of material. In the first type the nodules are spherical. In Figure 1 the nodules are composed entirely of pyrite. Figure 2 shows alternating bands of pyrite and marcasite; the marcasite is rather coarse-grained in this instance as is betrayed by the anisotropism. In the other type the nodules tend to be elongate or cigar shaped. In the example shown in Figure 3 the marcasite has been etched black with 1:1 HNO_3. These two types are fairly distinct and I do not think that type one is merely a circular cross section of type two.

More marcasite than pyrite appears to be present, although the relative amounts vary from specimen to specimen. The intimate mixture of pyrite and marcasite may be due to an oscillation of pH above and below 7.

Terminology for this variety of FeS_2 is somewhat confusing and it is time the problem was cleared up. The trouble seems to hinge on the question of what is melnikovite. Ramdohr (5) defines melnikovite-pyrite or gelpyrite as a crystallized gel of FeS and $FeS_2 \pm$ As which now consists mainly of pyrite, but still contains small amounts of FeS, As and perhaps H_2O. He makes no distinction as to place of formation. Also, he refers to the "birds-eye" structure formed by weathering of FeS and mentions that the products may be either marcasite or pyrite, but this still does not give a proper terminology.

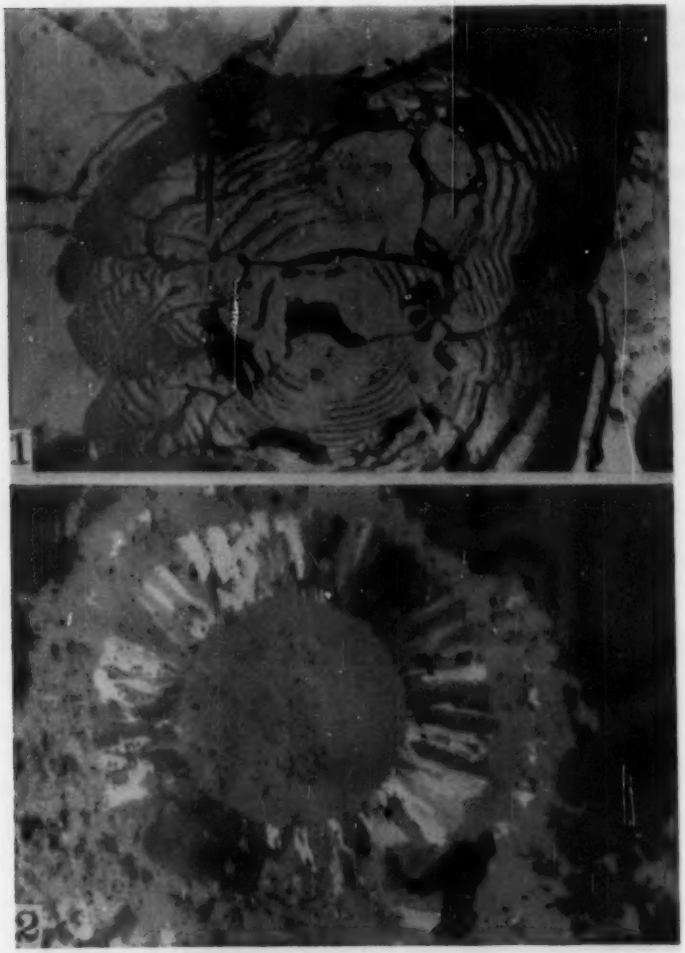

FIG. 1. Concentric FeS_2 in pyrrhotite. Note concentric cracks. × 84.
FIG. 2. Nodule of secondary pyrite and marcasite. × 250. x-Nicols.

Uytenbogaardt (9) defines melnikovite-pyrite as "concentric or radiated aggregates of micro- or crypto-crystalline, may be partly amorphous, substance consisting of pyrite and marcasite, commonly also containing some As. The name should only be used when indicating such aggregates and not as a mineral name." Furthermore, he defines melnikovite as "black, finely divided pyrite, regarded as having been derived from iron sulphide gel."

Edwards (2) also refers to melnikovite-pyrite and states that it is formed from melnikovite by alteration.

It is evident that no real unanimity exists. Furthermore, terms such as melnikovite-pyrite or melnikovite-marcasite are commonly used as more or less structural terms, alluding to the concentric nature of the aggregate.

Lepp's (3) experiments seem to re-establish melnikovite as a mineral in its own right. This mineral was discovered by Doss in Miocene clays and

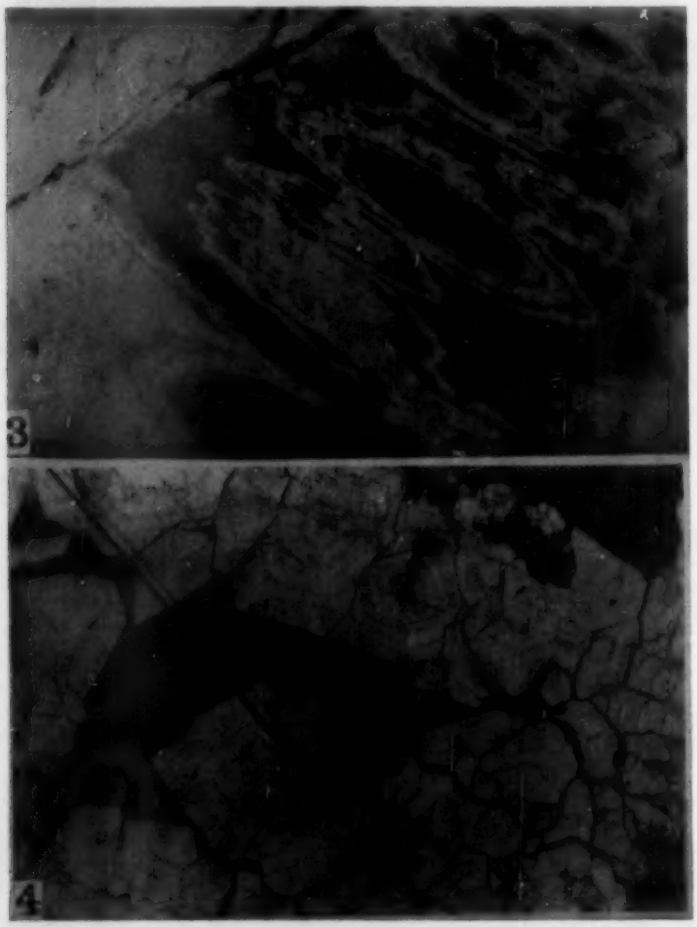

FIG. 3. Cigar-shaped areas of concentric FeS_2 in zoned pyrite. Marcasite etched black with 1:1 HNO_3. × 84.

FIG. 4. Zoned pyrite. Etched. × 84.

was described by him in 1912 (1); Lepp has produced it synthetically. Melnikovite is black, cryptocrystaline, magnetic, soluble in dilute HCl and exhibits colloform structure. It has an Fe-S ratio of approximately 1:2 and alters to pyrite. Both Doss and Lepp consider it to be a product of chemical sedimentation under reducing conditions, such as those that exist in barred basins.

It is clear, then, that terms involving the name melnikovite should be applied only where melnikovite can be proved to be a forerunner of the pyrite or marcasite being considered; they are genetic terms and not structural terms, although structure of some sort may be implied. There is no evidence that the concentric FeS_2 at Nairne has been derived in any way from melnikovite; it is a secondary alteration product and should not be confused with the melnikovite of Doss and Lepp. Nairne is not the only such case of pyrite and marcasite formation—compare Newhouse (4), Schwartz (6, 7), and Weston-Dunn (10)—and, until a more appropriate term is proposed, it is the author's opinion that such aggregates should merely be referred to as concentric FeS_2, which is a structural, not a genetic term. Some degree of genesis may be indicated by employing such terms as primary concentric FeS_2 or secondary concentric FeS_2.

Zoned Pyrite.—In a number of instances the pyrrhotite appears to be altered to a more or less rectangular boxwork, and from the walls of this boxwork project small crystals of pyrite. This phenomenon is found in all stages of development and the crystals are not uncommonly .5 cm across; the long dimension of a "box" may reach 1.5 cm but .5 cm is more the rule. It is common to find boxworks still containing remnants of pyrrhotite. These boxworks are especially well developed in the large pyrrhotite masses in the large veins and have been found as deep as 450 feet below the surface.

In polished section the pyrite crystals are found to be isotropic and to consist of alternating zones of darker and lighter material (Fig. 4). The lighter material is slightly more brownish than regular pyrite and forms the thickest zones. The darker material is even more brownish and forms thin zones between the light zones. The outlines of the zones are essentially isometric but need not necessarily follow the external outline of the crystal.

Not uncommonly the zoned pyrite will have as its "core" an area of concentric FeS_2. More recently examples have been encountered in which veinlets of zoned pyrite cut masses of concentric FeS_2. These observations suggest that the zoned pyrite, at least in some instances, forms from the concentric FeS_2.

The analyses of these two forms of secondary FeS_2 show:

	Fe	S	Ni	Co	Mn	Ti
C. FeS_2	46.0	50.3	.15	.02	.07	.02
Z. P.	46.0	48.4	.13	.03	.05	.07

Recalculating the Fe-S ratios to 100 percent gives a formula of $FeS_{1.91}$ for the concentric FeS_2 and a formula of $FeS_{1.84}$ for the zoned pyrite. The composition of the zoned pyrite falls far below the accepted lower limit for pyrite

($FeS_{1.94}$). The reason for this is not understood at present; caution must be exercised in evaluating such a limited number of analyses. The Co and Ni may be responsible for the darker zones, as in bravoite.

As regards origin the following is certain: The main mass of secondary FeS_2 has formed by the action of weathering; perhaps all of it has formed in this way. The amount of secondary FeS_2 rapidly diminishes with depth so that below the zone of obvious weathering, only veinlets and seams of altered pyrrhotite are found. These are, however, especially conspicuous in the large veins containing the Ag-Sb minerals. It is therefore suggested that the alteration visible at depth may be a product of late hydrothermal solutions. These solutions would be relatively "cold" and would tend to affect the pyrrhotite in the same way as would weathering. It is, however, not impossible that the effects of weathering continue down over 400 feet.

FeS_2 from Circulating Ground Water

In a few areas of the quarry, cracks have opened, and solutions formed during weathering have trickled down, altering the country rock and depositing various minerals. A common sequence of deposition is zeolite, siderite, limonite var. esmeraldite, and patches of FeS_2 in small (less than .15 mm across) crystals. Polished sections show a concentric structure and layers of intermixed pyrite and marcasite.

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STRUCTURAL BELTS AND MINERAL DEPOSITS OF NORTHWESTERN ARGENTINA

F. B. WHITING

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ABSTRACT

In northwestern Argentina three belts that differ in topography differ also in structure, in type of igneous activity, and in their mineral deposits. The belts trend northnortheast parallel to the main line of the Andes Mountains.

The easternmost belt is a lowlying area of gentle folds, with a fairly complete stratigraphic section, no acidic intrusives, very little basic intrusive rock, no volcanic activity, and few metal deposits.

The central belt is a zone of strong regional thrust-faulting and uplift, and is the main zone of movement between the lowlands to the east and the high Andean plateau to the west. The sedimentary column is less complete, as the area was uplifted during much of geologic time. Granitic intrusions are spread throughout the belt. Late volcanic activity is lacking. Mineral deposits consist of numerous veins and one replacement deposit, with lead, zinc, silver, copper, barite, and other metals. The Aguilar mine, largest in Argentina, is situated within this belt.

The westernmost belt is a high plateau with many Precambrian areas, a scanty Palaeozoic and Mesozoic section, and abundant volcanos. Late granites are absent. Mineral deposits are copper and iron, associated with Precambrian granodiorites, and silver, tin, gold, antimony, borax, and sulphur, associated with the young volcanic rocks.

INTRODUCTION AND ACKNOWLEDGMENT

THE information presented in this paper has been accumulated by the writer over the period 1954–1958, partly from publications, which are mentioned in the references, and partly from his own observations on many mine examination trips throughout the area. Most of the information on stratigraphy was taken from H. J. Harrington's report (3) on Argentina. It is unfortunate that, although much of the area described has been studied in detail,

the maps and reports have not been published, or were not available to the writer. The abbreviated map of the regional geology was pieced together from various sources, and where information is given, it is thought to be reliable. Extensions into unmapped areas are shown by broken lines, and may be somewhat in error. Suggestions and interpretations were given, and extra data made available, by J. R. Cuomo, R. R. Fernández and C. R. Prozzi of the geological staff of Cía. Minera Aguilar. Part of the regional geology of the area was compiled by W. C. Stoll. The writer wishes to thank the management of Cía Minera Aguilar and of St. Joseph Lead Co. for permission to publish this paper.

TOPOGRAPHIC BELTS

In northwestern Argentina, an area which for the purposes of this paper includes the provinces of Jujuy, Salta, and the northern part of Catamarca, three distinct topographic belts exist. These belts trend generally north to

FIGURE 1 : LOCATION MAP

north-northeast in conformity with the structural lines of the Andes Mountains. Figure 1 shows the area discussed.

The easternmost belt is known as the area of the Sub-Andean Ranges. It is a zone of wide valleys and low rolling hills, lying between 300 and 2,500 meters above sealevel. The climate is tropical to sub-tropical. Agriculture flourishes, particularly where aided by irrigation. This belt merges eastward into the flat Chaco area, and westward into the edge of the Andes proper. It is about 110 kilometers wide.

The central belt is known as the Eastern Cordillera. It is a zone of steep mountain chains, separated by deep valleys. The range of elevations is

great, as the lower parts of the valleys drop down to 1,300 meters above sealevel, and the mountain peaks reach up to 6,200 meters above sealevel. The general level is about 4,000 meters. Agriculture is confined to the protected valley bottoms. The climate is arid and cold, with strong winds. This belt is 70 to 130 kilometers wide.

The western belt is known as the Puna area. It is a high plateau, with interior drainage, lying at a general elevation of 3,900 meters above sealevel. High volcanic peaks are scattered over all this area, reaching up to elevations of as much as 6,700 meters above sealevel. The climate is arid and cold. This belt is 90 to 240 kilometers wide in Argentina, but extends west for considerable distances into Chile and southwestern Bolivia.

REGIONAL STRATIGRAPHY

Precambrian.—No extremely old Precambrian beds are recognized. All the sediments are placed in the middle Precambrian, and consist of slightly metamorphosed shales, sandstones and graywackes. Granitic and granodioritic intrusives are present in all the known Precambrian areas.

Palaeozoic.—The Cambrian beds consist of generally unfossiliferous bright-colored sandstone and shale. Worm tubes may be present. These beds lie with strong angular unconformity on the Precambrian sediments and granites. The thickness of the Cambrian sediments is extremely variable in this part of Argentina, as they form a wedge, 1,500 ms thick in the east, thinning sharply towards the west to 400 m in the Eastern Cordillera, and wedging out entirely in the Puna area.

The Ordovician, called Lower Silurian in Argentine terminology, is a very widespread formation having a maximum thickness of about 2,400 m. The rock types are: at the base, generally a green, gray, or black shale, with some thin limestone layers, and many trilobites, about 300 to 500 m thick; above this, 1,000 to 1,450 m of shale, with graptolites; above this, 500 to 600 m of limestone and marl with molluscs and brachiopods or shale with graptolites, depending on the area; above this, 400 m of yellowish sandstone with worm tubes and "Lingula." The uppermost layer is found only in the Sub-Andean Ranges.

The Silurian is found only in the Sub-Andean Ranges, where it is represented by 300 m of sandstone, with graptolites, lying with slight unconformity on the Ordovician. These beds are classified as Middle Silurian.

The Devonian, also, is found only in the Sub-Andean Ranges, and consists of shale with some sandstone and conglomerate, totalling 800 m in thickness. It contains "spirifers." It lies with slight unconformity on the Silurian.

Mississippian and Pennsylvanian beds are absent in this part of Argentina.

The Permian here consists of 1,000 m of mixed sediments, including 150 m of tillite at the base, lying unconformably on the Devonian shales, followed by shale and sandstone.

Mesozoic.—Owing to poor fossils in the Mesozoic beds, and to the lack of a Jurassic section, there has existed considerable disagreement among geologists who have studied this area as to whether the following beds are Triassic

or Lower Cretaceous in age. The latest work seems to indicate a Lower Cretaceous age. The "Lower Sandstones" are 1,200 m of red-violet sandstone with thick beds of conglomerate and some basalt flows. Above these beds lie 400 m of dolomitic limestone with sandstones and marls, called the "Lime-Dolomite Horizon."

Above these beds lie Upper Cretaceous shales, marls and sandstones, 1,200 m thick, known locally as the "Margas Multicolores."

Cenozoic.—The Eocene, Oligocene and Lower Miocene are not represented in this part of Argentina.

The Upper Miocene beds, the "Upper Sandstones," are a continental series 600 to 1,200 m thick, consisting of varicolored sandstone, shale, and one limy layer. In the Puna area, some volcanic rocks are of this age.

The Pliocene beds consist of 4,000 m of sandstone and shale, with andesitic tuff interbeds, and, in the Puna area, widespread flows. The uppermost part, the Jujuy Beds, consists of several hundred meters of conglomerates with sandstone and shale, and is regarded as uppermost Pliocene.

Quaternary and Recent sediments consist of valley fill, terraces, lateral moraines and outwash fans.

In summary, each of the three topographic belts has a different section of sediments. The Sub-Andean area has the most complete sedimentary section, including Precambrian, marine Cambrian, marine Ordovician, marine Silurian, marine Devonian, continental Permian, continental or brackish-water Lower Cretaceous and continental Upper Cretaceous, and continental Miocene, Pliocene, and Quaternary-Recent beds. The Eastern Cordillera has a thinner, less complete section consisting of Precambrian, thin marine Cambrian, marine Ordovician, continental and brackish-water Lower Cretaceous and in part Upper Cretaceous, continental Miocene, Pliocene and Quaternary-Recent. The Puna area has Precambrian, thin or no Cambrian, abundant Ordovician, possibly some Lower Cretaceous, and widespread volcanic Miocene, Pliocene, and Quaternary-Recent deposits.

INTRUSIVE ROCKS

The Sub-Andean belt has no late intrusive granitic rocks, few basic dikes, and only a small amount of extrusive volcanic material incorporated in the sediments.

The Eastern Cordillera has numerous Mesozoic or Tertiary granites, and more basic dikes, but very little extrusive volcanic material. The Puna area has, as far as is known, no granites later than Precambrian, but does have huge amounts of extrusive volcanic material from Miocene to Recent in age. Several small dacite intrusions of Miocene age occur in the Puna area, and one is known in the Eastern Cordilleras. The term "granite" is used here to cover a wide variety of acidic intrusives, grading from true granites through granodiorite to quartz monzonite. Generally these bodies, where they are of post-Precambrian age, are small, ranging from one to 250 square kilometers in area. The Precambrian granites and granodiorites cover larger areas, in places ranging up to 600 square kilometers. The age of the later intrusives

is not known. Some authorities give them a Palaeozoic or Mesozoic age. The writer is inclined to believe that the majority of them are late Tertiary. As they occur in areas where the youngest exposed rocks are Ordovician, direct dating is difficult. However, at the Aguilar mine, there is evidence that a stock of this type, though cut by faults that cut the Upper Cretaceous and Upper Miocene beds, was intruded just prior to the main period of faulting. Furthermore, at least two of these granites are intruded into the

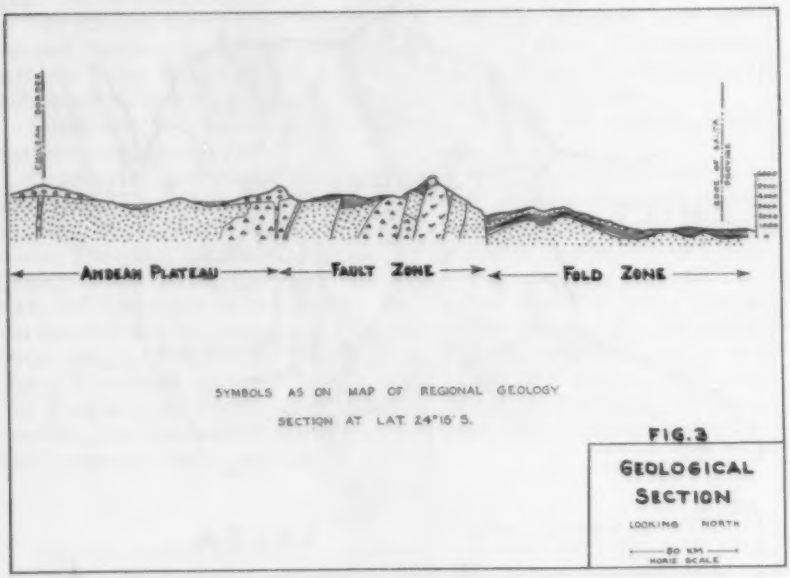
FIG. 2

centers of dome structures in the Ordovician beds, and as the domes date from the Tertiary, the granites probably belong to this period as well.

STRUCTURAL BELTS

The three topographic belts mentioned previously correspond to three zones each with a different basic structure. The regional geology of this part of Argentina is shown, abbreviated, in Figure 2.

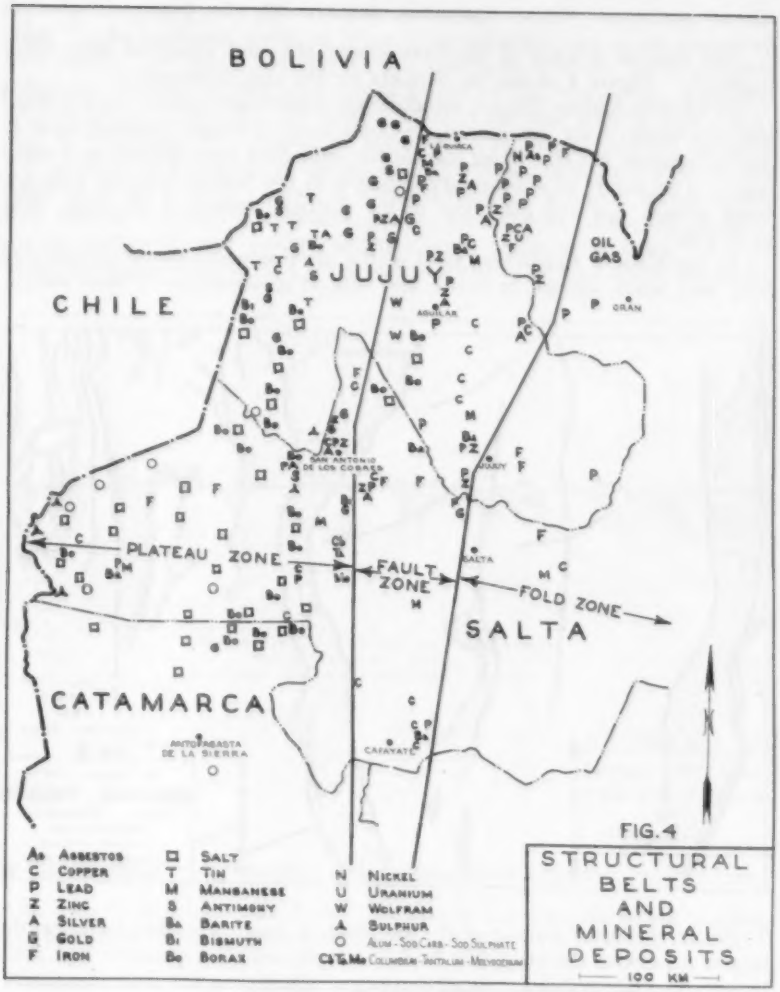
In the Sub-Andean Ranges the basic structures are gentle northnortheast-trending folds, cut in places by axial-line faults with small movements, and by minor cross faults.



The Eastern Cordilleras are a zone of strong thrust faulting, doming, and overturning. The faults strike generally northnortheast, and dip steeply to the east or to the west. This belt is the zone of movement between the uplifted Andean Plateau to the west and the lowlying area to the east. Vertical displacements of 5,000 to 10,000 m are common. For example, west of the city of Jujuy, Pliocene-Miocene beds are faulted into contact with Precambrian strata, so that the fault must have a vertical displacement of about 11,000 m.

The Puna area is a high plateau, cut by a few north-trending faults, which are thought to be mainly of the block-fault type.

The age of the folding and faulting, ignoring minor movements in the Palaeozoic, was progressively younger from west to east. In the Puna, block



faulting started in the Middle Miocene, was renewed in late Miocene time, continued irregularly throughout the Pliocene, and decreased during the Quaternary. In the Eastern Cordilleras, movement began in the late Miocene, continued in the Pliocene, and attained its maximum, with great uplift, between the Pliocene and the Quaternary. In the Sub-Andean Ranges the faulting began in the late Pliocene and continued into the Quaternary.

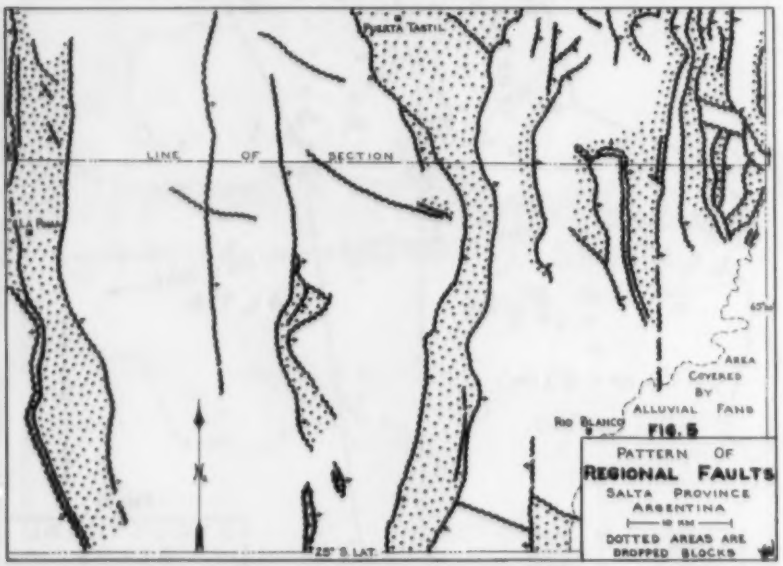
Figure 3 is an east-west profile showing these three belts.

MINERAL DEPOSITS

The mineral deposits of the three topographic and structural belts differ markedly. Figure 4 shows the deposits for the area discussed.

In the Sub-Andean Ranges, metalliferous deposits are scarce. A few small lead-zinc-silver veins are known, and one area of copper impregnation in sandy limestone exists. Some manganese veins have been worked on a small scale. Two layers of sedimentary hematite in the Middle Silurian beds are being mined. Oil and gas occur in the northeast corner of the area, close to Bolivia.

In the Eastern Cordilleras most of the metal deposits are veins carrying lead, zinc, silver, copper, or barite, and various combinations of these metals.



Typically, the silver content of the lead veins is low. The Aguilar mine, the largest deposit of the area, is a lead-zinc replacement in quartzite and shale between two late granites. Small deposits of asbestos, nickel, iron, manganese, uranium, wolfram, and gold occur. Borax is mined from one lake bed close to the western border of this belt. The metalliferous deposits appear to be associated with the late granites, and with zones of strong faulting.

In the Puna area most of the mineralization is associated either with the Precambrian granites or with the Tertiary-Quaternary volcanic intrusives and extrusives. Iron and copper occur as replacements and veins in the Precambrian granites, and pegmatites of the same age in Salta province carry molybdenum, columbium (niobium), tantalum, and some bismuth. The

deposits associated with the volcanic rocks vary widely depending on the area. In the northwest corner of Jujuy, gold, antimony, and tin are associated with dacites, and borax and sulphur are associated with the latest andesitic volcanos. Slightly further southeast is a zone of lead with silver, gold, and silver with tin. Typically, the silver content of the lead veins is high. Several of these deposits lie close to Miocene dacite plugs. Similar deposits, also close to or within dacite plugs, occur northwest and southwest of San Antonio de los Cobres. Borax is found throughout the area in salt basins with interior drainage and in seepages on the hillsides. Deposits of alum, sodium carbonate, and sodium sulphate occur in volcanic areas. A zone of antimony-gold-bismuth lies south of San Antonio de los Cobres, associated

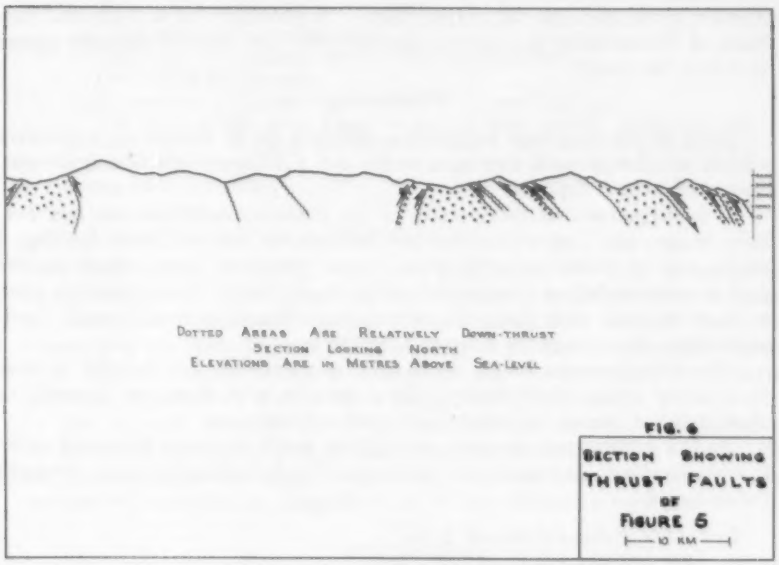


FIG. 6
SECTION SHOWING THRUST FAULTS OF FIGURE 5
10 KM

with early Tertiary andesite flows. Sulphur is found on the recent volcanos that form the Chile-Argentina border.

FAULTS AND VEIN SYSTEMS

Figure 5, which is an enlarged view of the small rectangle in the center of Figure 2, shows the pattern of faulting in the thrust belt. Dotted areas in this illustration are down-faulted blocks. It should be noted that the westernmost strip, with the town of La Poma in its center, is a down-thrust, rather than dropped graben-type block, as the bordering faults dip outward, not inward. Figure 6 shows a vertical section across this area. The thrust faults dip both east and west. The other feature of interest in Figure 5 is the

existence of a set of cross faults. These belong to the same age as the main north-trending thrusts, as they both cut and are cut by the thrusts. Three directions of the minor cross faults can be recognized. The main set strikes westnorthwest; a secondary set strikes northeast. The last, and least common, set strikes northnorthwest, in places nearly parallel to the main thrusts.

As can be seen in Figure 2, the veins in this part of Argentina conform in abundance and strike with these three groups. The most prolific group of veins strikes N60°W to N80°W, and are clustered within the thrust-fault belt. Less abundantly, the veins strike northeast or northnorthwest. In and near the fault belt are a few veins that are parallel to the main line of thrusting. Veins that strike due north, in Precambrian rocks, generally follow structural lines that were established in Precambrian time, long before the division of the area into the present belts. A secondary set of folds and fractures of Precambrian age strikes east-west, but few mineral deposits appear to follow this trend.

CONCLUSIONS

Each of the structural belts has a different set of sediments, a different variety of intrusive and extrusive rocks, and a different selection or concentration of mineral deposits.

It is suggested that the granites of the Eastern Cordilleras are late Tertiary in age, and rose within that belt because the zone of thrust faulting, a major zone of weakness in the crust, tapped the lower levels where granitic rock became mobilized concurrently with the faulting. These granites seem to have brought with them the widespread, though generally small, lead-zinc-copper deposits of the Eastern Cordilleras.

The volcanic rocks of the Puna area, further west, are thought to have risen along major block faults. They brought with them the deposits of alum, sulphur, borax, tin, silver, gold and antimony, etc.

As is a general rule in many parts of the world, the veins here tend to lie in cross fractures associated with, and caused by, but diverging from, the main thrust faults.

Compañía Minera Aguilar, S. A.,
Tres Cruces, Jujuy, Argentina,
Oct. 14, 1958

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AN X-RAY STUDY OF LEUCOXENE FROM QUILON, INDIA

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ABSTRACT

The commercial leucoxene concentrate from Quilon has been studied by X-ray diffraction methods. This concentrate consisted primarily of the altered grains of leucoxene and some unidentified black grains. The leucoxene grains, depending on their color were hand-picked into three fractions, which were analyzed to contain chiefly,

(i) rutile and pseudobrookite
(ii) rutile and pseudobrookite with some anatase
(iii) rutile and anatase

Small amounts of hematite were found in all the fractions.

The black grains were found to be a mixture mainly of anatase and pseudobrookite. These grains also contained a few ilmenite grains, most probably carried over as a mechanical impurity. Ilmenite was not found in any other fraction.

INTRODUCTION

THE beach sands of Quilon, India, are well known for their monazite and ilmenite contents. During the magnetic separation of the minerals, monazite and leucoxene concentrate together. The separation of monazite from leucoxene is a laborious process and after several gravity and magnetic separations an almost monazite-free leucoxene fraction is obtained, which is either marketed separately or is often taken along with the ilmenite.

The magnetic behavior of the Quilon leucoxene cannot be explained on the basis of the generally current ideas regarding the composition of leucoxene, and since no study had been made of the leucoxene from these sands, it was decided to investigate its composition by X-ray diffraction methods.

PREVIOUS WORK

The term "leucoxene," according to Dana (4, p. 560) is loosely applied to "dull, fine-grained yellowish to brown alteration products high in titanium" and believed to have been obtained from either sphene, ilmenite, perovskite, titanian magnetite or other titanium minerals. Its nature and chemical composition are known to be variable (1, 11), yet leucoxene is commonly considered (2, 3, 4, 8, 11) to be microcrystalline rutile only. Occasionally some leucoxenes have also yielded X-ray patterns corresponding to either sphene (1), brookite (1, 3, 11), anatase (11) or mixtures of rutile with anatase or brookite (3).

In 1954, Lynd, Sigurdson, North and Anderson (8) studied the commercial ilmenite concentrate from several localities. From X-ray powder data they showed that the Quilon concentrate consisted of ilmenite, hematite,

and rutile only. They concluded that all the non-ilmenite portion of the concentrate consisted of a porous mixture of fine grained rutile and iron oxide formed as result of the alteration of ilmenite. In 1956, Bailey, Cameron, Spedden and Weege (2), studied the alteration of ilmenite to leucoxene taking place naturally in the beach sands of several localities, but not including Quilon. They identified three distinct stages of alteration, the final stage—leucoxene, being only finely crystalline rutile commonly in the form of oriented aggregates. In a subsequent communication Bailey et al. (3) have reported that a number of leucoxene grains also yielded X-ray photographic patterns corresponding to mixtures of rutile with anatase or brookite. From this it is obvious that leucoxene should be as magnetic as any of the polymorphs of titania and should therefore concentrate with rutile in any magnetic separation.

PROCEDURES ADOPTED

Since the ilmenite fraction from Quilon had already been studied by Lynd et al. (8) it was decided to study the commercial leucoxene concentrate only. This enabled the study of compositional variations if any, in the "leucoxene" from the same locality.

The original concentrate as received, contained in addition to the pale yellowish to dark brown alteration products, some rutile, quartz, and zircon grains that were obviously mechanically carried over. It was surprising however to find that the concentrate also contained an appreciable amount (ca. 30%) of totally black grains. The identity of these grains was then not known, but it seemed very unlikely that these could be the original ilmenite.

To obtain a purer sample, the grains of the alteration products were handpicked under the microscope. Based on their color in reflected light and the amount of black streaks then believed to be unaltered ilmenite (7), the altered grains were separated into three fractions:

(i) almost black to dark-brown, showing few brownish streaks commonly on an all black background. These were then thought to represent the very slightly altered ilmenite grains probably corresponding to stage one—patchy ilmenite, reported by Bailey et al. (2).
(ii) yellowish brown with few black streaks or individual black patches.
(iii) pale yellowish to yellowish brown, but without any black streak or patch, at least on the surface.

The powders of these grains, prepared for X-ray diffraction studies, exhibited a pronounced color variation, corresponding respectively to: (i) dark brown, (ii) pale brownish yellow, (iii) almost white. Consequently, the three fractions are referred to in all subsequent discussions as—"brown" "intermediate" and "white" leucoxene, respectively.

The unidentified black grains were separately collected and studied.

The X-ray powder patterns were obtained on a Philips Wide-Angle goniometer (G.M. counter diffractometer) following standard practices. In some cases, regular Debye-Scherrer photographs as also the X-ray patterns of individual single grains were photographed on a standard G.E. powder

camera of 144 mm diameter using filtered CuKα radiation. Film shrinkage corrections were calculated from a pattern of pure calcite.

DISCUSSION OF RESULTS

Original Concentrate.—The X-ray pattern showed the presence primarily of anatase and rutile, together with some quartz and probably also hematite and pseudobrookite. It was obvious that the fraction contained neither ilmenite nor arizonite, at least not in amounts sufficient to register an X-ray pattern. Arizonite is believed (10) to be weathered ilmenite and has been previously reported (5, 9) to be an essential constituent of the Quilon sands. The absence of ilmenite was most perplexing, as previously ilmenite patterns had been observed (2) in what were considered the slightly altered grains. This absence, however, confirmed the belief that the black grains so abundantly present in the concentrate were not ilmenite.

The other intriguing features of the pattern were the unusually large amounts of anatase and the probable presence of pseudobrookite. These obvious anomalies resolved themselves, when the various fractions were analyzed.

Brown Leucoxene.—The X-ray patterns of all the hand-picked fractions clearly showed that none of them corresponded to a single compound but all consisted of mixtures of rutile, pseudobrookite and small amounts of hematite.

In all previous X-ray analyses of leucoxene, pseudobrookite was never reported as one of the constituents. In some cases brookite has been reported. It should be mentioned that here also the preliminary results obtained by the photographic method indicated the presence of rutile and brookite with very faint hematite lines in some purposely overexposed photographs.

Even though the d-spacings of brookite and pseudobrookite are sufficiently close, so as to be confused with one another in X-ray photographs—particularly if the camera radius is small, they are sufficiently far apart to be uniquely distinguished by the counter diffractometer. The presence of pseudobrookite was established from the diffractometer patterns and also from the fact that only pseudobrookite and not brookite has the first line at 4.90 Å. Subsequent X-ray photographs of the individual grains in the large G.E. powder camera clearly showed the 4.90 Å line of pseudobrookite, and further showed that rutile and pseudobrookite were present as oriented aggregates.

It was also observed that the peak height intensities of the pseudobrookite and rutile lines varied slightly in the different samples. From the study of individual grains it was found that this ratio of pseudobrookite to rutile increased or decreased depending upon whether the grains were almost black or had a tendency to be dark-brown. Yet the average ratio of pseudobrookite to rutile was about 1 : 1.5 and was estimated by comparing the ratio of the peak heights of the 3.48 Å pseudobrookite and 3.24 Å rutile lines with those obtaining in appropriate artificial mixtures.

Only faint indications of the presence of hematite were obtained in the diffractometer patterns. Because the same lines were also observed in purposely overexposed powder photographs, it was concluded that hematite was present in small amounts. From the peak heights of the 2.69 Å line of

hematite and the 3.24 Å line of rutile, it was estimated that the ratio of hematite to rutile was about 1:7. In the samples examined, this ratio varied between about 1:6 and 1:8 with a bias towards 1:7.

From these results, it was concluded that these grains of brown leucoxene were a mixture of hematite, pseudobrookite and rutile in an average molar ratio of approximately 1:5:7.

No trace of ilmenite could be observed even in the grains that were thought to constitute the first stage of alteration. This absence indicated that in those grains either the composition of ilmenite had been completely altered or the ilmenite lattice only had been so thoroughly distorted as to render it almost amorphous (non-crystalline). However, the sharp patterns obtained did not give cause to believe that any amorphous or crypto-crystalline phase was present. It was therefore concluded that ilmenite had been completely altered and hence was absent in these grains. Their black color was then obviously due only to the mineral pseudobrookite.

"Intermediate" Leucoxene.—These were found to contain rutile, anatase, pseudobrookite, and very small amounts of hematite. Again no evidence was obtained for the presence of ilmenite. The few black streaks and patches could be attributed either to pseudobrookite or anatase or both. The relative ratio of pseudobrookite to anatase or their individual ratios with respect to rutile were not estimated, but it was obvious that the amount of pseudobrookite was considerably less than in the brown leucoxene.

"White" Leucoxenes.—In most of these samples, no pseudobrookite was detected, the diffractometer patterns showing the presence of only rutile, anatase and very little hematite. A few samples did show very faint indications of the 4.90 Å line of pseudobrookite. From photographs of the individual grains, it was further ascertained that a number of them consisted of rutile only and that only a small number consisted of both rutile and anatase. None of the individual grains showed the presence of pseudobrookite. It was concluded that the very weak 4.90 Å line of pseudobrookite observed in a few of the diffractometer patterns was probably due to inadvertent inclusion of the "intermediate" leucoxene grains during the hand picking.

Even though no hematite lines were observed in the photographs of the individual grains it was presumed to be present in all of them. This was confirmed by a spectrochemical analyses of these grains, which showed the presence of Fe and Ti only.

In samples where the presence of anatase was indicated in the X-ray pattern, it was confirmed by heating those samples in air at 1,000° C for 24 hours, thereby affecting the phase transformation of anatase to rutile. In the subsequent X-ray pattern, the anatase lines were completely absent and the rutile lines had enhanced intensities.

Black Grains.—From the X-ray photographs of several individual grains, it was found that most of these were of anatase, some of pseudobrookite, and only very few of ilmenite. From this observation on a small number (about 15) of the black grains, it was estimated that the ilmenite content in the original concentrate should be roughly about 1 percent. This presence could be attributed to the mechanical carry over in the industrial operations.

It was obvious, therefore, why no ilmenite lines were detected in the diffractometer patterns of the original concentrate, as well as why an unusually large quantity of anatase was found.

CONCLUDING REMARKS

Apart from the very small amounts of ilmenite in the black grains indicated by X-ray analysis, its absence in all the hand-picked fractions was noteworthy. This implied that the ilmenite lattice was destroyed very early in the process of alteration, a fact substantiated in the subsequent study (6) of the oxidation of ilmenite under controlled conditions in the laboratory.

The presence of hematite in all the fractions clearly revealed that it was a definite constituent of leucoxene. This fact, indicated even in the preliminary X-ray photographs, was made use of by the Ore-dressing section of this Establishment in the development of a new ore beneficiation method (7) for the rapid separation of monazite and leucoxene. A reducing roast of the monazite-leucoxene concentrate, reduced the Fe_2O_3 to Fe_3O_4 thereby considerably enhancing the magnetic susceptibility of the leucoxene grains, thus enabling a rapid and clean magnetic separation from the monazite.

The magnetic behavior of the original leucoxene concentrate could now be readily understood, since leucoxene was found to be a mixture of not merely the various polymorphs of titania, which are non-magnetic, but in addition also of hematite and pseudobrookite, both of which are paramagnetic. The magnetic susceptibilities of synthetic pseudobrookite and hematite, and of the original and reduced leucoxene concentrate, as well as of an average monazite sample from Quilon, were measured in a Guoy-type balance at 30° C:

Sample	Gm—susceptibility × 10⁶
Synthetic pseudobrookite	32.28
Synthetic hematite	19.16
Original leucoxene concentrate	3.57
Reduced leucoxene concentrate	55.21
Average monazite	10.32

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ATOMIC ENERGY ESTABLISHMENT TROMBAY,
BOMBAY, INDIA,
Oct. 20, 1958

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THE EFFECT OF METAMORPHISM ON METAL DISTRIBUTION NEAR BASE METAL DEPOSITS

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ABSTRACT

Sedimentary rocks near three base metal deposits were analyzed to determine possible changes in Zn, Cu, and Fe content caused by alteration or contact metamorphism.

In the Hanover, New Mexico, district of "contact metasomatic" Zn-Cu deposits, of the sediments only the Devonian (Percha) fissile shale contains sufficient Zn (70 ppm Zn, 48 ppm Cu, and 4% Fe) to contribute significantly to the metal content of the deposits. However, this shale has the same metal content (within ± 20 ppm Zn and Cu and within ± 1% Fe) when unaltered as in the recrystallized and silicified contact zone (excluding the skarn). Extraction of 20 ppm Zn from the altered area of the shale is quantitatively insufficient to account for the 600,000 metric tons Zn (18) in the skarn and ore deposits of the contact zone.

In the northern Mississippi Valley district, neither the Maquoketa shale (35 ppm Zn, 65 ppm Cu, and 3% Fe) nor the oil rock (20 ppm Zn, 60 ppm Cu, and 7% Fe) has a sufficient metal content in comparison with the background level given by average igneous rock (100 ppm Zn, 70 ppm Cu, and 5% Fe) to be the source for the metals in the deposits.

Near the margins of the San Francisco del Oro district, Chihuahua, Mexico, the gradient of Zn content from the veins into the silicified wall

rocks passes through a minimum below that of unaltered shale (123 ppm Zn, 75 ppm Cu, and 5% Fe). However, the quantity of zinc shown by this gradient to have been extracted from the shale is only a negligible fraction of the metal content of the entire deposit.

It is quantitatively impossible for the metal content of these three districts to have been derived from the surrounding Paleozoic or younger sediments by lateral secretion.

INTRODUCTION

THE purpose of this study is to obtain geochemical data on the distribution of the metals in the vicinity of ore deposits in order to delineate source areas from which the metals might be derived.

The change in metal content caused by local contact metasomatism or by alteration of sedimentary wall rocks has been advocated as a source for the metals of base metal deposits. By the analyses of altered and unaltered sediments from districts where this hypothesis seems most applicable, it is possible to evaluate quantitatively this source in relation to ore production and reserves. Zn, Cu, and Fe are the metals most useful for such a study because they are sufficiently abundant to be accurately determined by analysis and their distribution and characteristics in ore deposits are relatively well known.

Because there are insufficient data available in the literature for the present purpose, over 136 rock samples have been analyzed from three ore deposits representing a contact metasomatic type, a vein type, and a Mississippi Valley type deposit.

DISTRIBUTION OF BASE METALS IN ROCKS

Source rocks for the base metals may obviously be either of high metal concentration and relatively small volume or of lower concentration and large volume. By examining the distribution and character of the rock types high in metal content, the more probable type of source may be selected (Table 1).

Although the number of analyses on which Lundegårdh's Zn values (given in Table 1) are based are very small, they agree quite well with those of Wedepohl (21) and Sandell and Goldich (17) despite the lack of interlaboratory calibration and despite possible regional variations in metal content. The values of Krauskopf for sedimentary rocks generally include within their limits the new analyses by Shaw (19) although a few analyses fall below the lower limit given in Table 1. Sufficient numbers of analyses of various rock types are available to select potential sources with high metal content even if the average given may be slightly in error.

The small spread and low average values of metal content of igneous rocks and sedimentary rocks with the exception of black shales (Table 1) shows that only relatively large volumes of these rocks could contribute sufficient metal for an ore deposit. Because the maximum Zn, Pb, and Cu content of black shales is 10, 25, and 4 times, respectively, that of average igneous rock, a relatively small volume of some black shales could supply the metals for a deposit if the content were reduced only to the general background level.

Lundegårdh (14) found 1,000 ppm (0.1%) Zn in the thin-bedded Cambrian Tessini shale. White and Wright (22) found 1–3% Cu in the thin-bedded late Keweenawan Nonesuch shale. Trask (20) gave the composition

(1.85% Zn, 3.24% Cu, 0.59% Pb) in his summary of the thin-bedded Upper Permian Kupferschiefer. The slightly metamorphosed "Ore Shale" of the Roan Antelope (6) deposit with an average 3.3% Cu is also of this type. Each of these deposits is thin-bedded, of large areal extent and remarkably constant in composition laterally with a high organic content. A shallow sea with very slow deposition of these shales is probably typical, with weathering of source lands predominantly chemical rather than mechanical. This environment is characteristic of the craton.

In order to investigate the possibility that local metamorphism might liberate metals (i.e., a form of lateral secretion) from a rich black shale source, three deposits containing one or more of the metals Zn, Pb, and Cu were selected where there was sufficient shale in the stratigraphic column to be a

TABLE 1

SULFUR AND BASE METAL CONTENT OF ROCKS (PARTS PER MILLION)

Igneous rocks	Zn (14, 15)			Pb (16) Average	Cu (16) Average	S (16) Average
	No. of samples	Spread	Average			
Peridotites						2,500
Pyroxenites						3,000
Gabbros	7	50–140	90	5		2,000
Basic igneous rocks				9	149	
Quartz diorite	5	70–200	120			1,000
Granodiorite, quartz syenite	7	160–250	200		38	
Granitic rocks	17	50–250	150	30		500
Acidic igneous rocks	7	<5–80	30	19	16	500
Average igneous rocks			100±20	16	70	520
Sedimentary rocks (range of values)		Zn (12)		Pb (12)	Cu (12)	S (12)
Sandstones		5–20		10–40?	10–40	300
Shales (average)		50–300		20?	30–150	2,600
Limestones and dolomites		4–20		5–10?	5–20	1,100
Black shales		100–1,000		20–400	20–300	—
Bauxite		120–360		7?	14?	—
Iron oxide sediments		173?		—	180?	—

potential metal source. These deposits represented a contact metamorphic type (Hanover, New Mexico), a vein type (San Francisco del Oro, Chihuahua Mexico), and a Mississippi Valley type replacement deposit (Shullsburg, Wisconsin). Both altered and unaltered samples were taken of the shales and other rocks about each deposit to note systemic changes in the metal content. The shales near the contact metamorphic and the vein deposits are black shales; the shales of the Mississippi Valley deposit are brown. Each district will be considered individually below.

ANALYTICAL TECHNIQUE

Cu and Zn were determined colorimetrically with dithizone on a Carey recording spectrophotometer. Fe was also determined colorimetrically but with HCl by visual comparison with standards. The analytical technique is

TABLE 2

STANDARD DEVIATION OF THE ANALYTICAL METHOD

	Range	Standard deviation
Zinc:	0–40 ppm	3 ppm
	40–100 ppm	8%
	100–200 ppm	9%
	200–500 ppm	10%
Copper:	at 250 ppm	3.5 ppm
Iron:	at 2%	26%

described elsewhere (2, 3) and the analytical error is given in Table 2. In this paper, the standard deviation (including *both* sampling and analytical error) is given for each Zn analysis but not for Cu and Fe for two reasons. Sampling and grain size studies (2) indicated that the variation in representative samples collected by standard techniques exceeded the analytical standard deviation for the Cu analyses, particularly in black shales. In the grinding procedure, small but erratic amounts of Cu and Fe were added to the sample. Both of these sources of error are unpredictable, but, fortunately, unimportant except at low concentrations. The effect of other elements on the error is negligible in the rocks analyzed (2, p. 90). Because both sampling and analytical precision were determined, it is expected that the absolute accuracy of the Zn analyses is described by Table 2.

ZN, CU, AND FE DISTRIBUTION IN PART OF THE HANOVER DISTRICT

General Description of the District.—The Hanover district, part of the Central Mining district, is located in southwestern New Mexico in Grant County about 130 miles northwest of El Paso, Texas. Structurally, the district is near the southern edge of the Colorado Plateau and on the northern edge of the Sonoran geosyncline. The combined thickness of Paleozoic and Mesozoic rocks is less than 5,000 feet (8, p. 119). Although the porphyry copper deposit of Santa Rita is nearby, the deposits of particular interest to the present study are contact metasomatic Zn-Cu-Pb-Fe replacement deposits adjacent to the Hanover granodioritic intrusive. In the sediments in successive bands outwards, a normal skarn zone, a zone of silicification and a zone of recrystallization surround the intrusive. Zoning of magnetite, chalcopyrite, sphalerite, and galena occurs within the ore bodies.

Detailed descriptions of parts or the entire district have been published by Schmitt (18), Hernon et al. (8), Lasky and Hoagland (13), Graf and Kerr (7), and a preliminary report of the U. S. Geological Survey is now in press. The stratigraphic section is described in Table 3 which is summarized from a U. S. Geological Survey open file report (9). The main ore horizon is near the base of the section and the extent of mineralization decreases upwards. On the basis of the spread of published metal abundances, the only potential sedimentary source of at least as much Cu, Pb, and Zn as is now found in the deposits should be the Ready Pay member of the Upper Devonian Percha shale.

Sample Locations.—Sample locations are shown by the numbered sections on the simplified geologic map of the district, Figure 1, and the stratigraphic

TABLE 3

PRE-TERTIARY STRATIGRAPHIC SECTION OF THE HANOVER DISTRICT[1]

		UNCONFORMITY		
Cretaceous	Upper Cretaceous	Colorado formation	<1,000 feet	About 800 ft of ss. and arkose alternating with some shale. At base about 200 ft of gray fissile shale.
	Upper (?) Cretaceous	Beartooth quartzite	50–140 feet	Fine-grained quartzite with thin shale partings.
		UNCONFORMITY		
Permian	Lower Permian (Wolfcamp)	Abo formation	0–640 feet	Red shale, siltstone and limy mudstone with conglomerate lenses.
		UNCONFORMITY		
Pennsylvanian	Magdalena Group	Syrena formation	170–390 feet	Silty limestone, limestone conglomerate and 10–40 ft of limy shale.
		Oswaldo formation	330–420 feet	Thick-bedded cherty limestone with few shale partings. A marker bed, 20–40 ft thick, of shale occurs at the base, the "Parting Shale member."
		UNCONFORMITY		
Mississippian	Lower Mississippian (Osage)	Lake Valley formation	300–400 feet	Basal member of 15–41 ft of thin-bedded crinoidal ls. Above this is a cliff-forming member (Alamogordo member), 20–44 ft thick, of thick-bedded ls. with masses of black chert; overlain by 170 ft of shaly ls., and a top member of about 100 ft of crinoidal ls. *This unit is the principal host rock of zinc ores.*
Devonian	Upper Devonian	Percha shale Box member Ready Pay member	250–315 feet	The lower Ready Pay member is black fissile shale with a few beds about ½ inch thick of argillaceous ls. and tan calcareous shale. The Box member consists of about 95 ft of limy shales with abundant fossiliferous ls. nodules up to 4 inches long. The limestone content of this formation increases upwards to about 100% at the top.

[1] Adapted from Hernon et al. (9).

TABLE 3—*Continued*

PRE-TERTIARY STRATIGRAPHIC SECTION OF THE HANOVER DISTRICT[1]

		UNCONFORMITY		
Silurian	Lower to Middle Silurian	Fusselman limestone	30–40 feet	Massive dolomite with sparse chert nodules; chief host of silver-lead ores near Georgetown.
Ordovician	Upper Ordovician (Cincinnatian)	Montoya limestone	370–470 feet	Basal unit is 1 to 28 ft of ss. grading upward into a sandy dolomite. A middle member, about 200 ft thick, is composed of massive dolomite with prominent chert horizons. The upper member, about 200 ft thick, is thin-bedded ls.
	Lower Ordovician (Canadian)	El Paso limestone	560 feet	Lower 400 ft, thin-bedded ls. or dolomite with abundant thin siliceous layers. Upper 100 ft is ls. with nodular chert becoming abundant in top few feet.
Cambrian	Upper Cambrian to Lower Ordovician (Croixian)	Bliss formation	146 feet	Conglomerate with boulders of Precambrian greenstone up to 4 ft long locally at the base. Overlain by dolomite, conglomerate, thin glauconite and ls. beds with shale partings.
		UNCONFORMITY		
Precambrian		Basement complex		Granite, gneiss, muscovite schist, greenstone, biotite spotted hornfels.

position of each sample is shown diagrammatically in Figures 2 and 3. The section near the Hanover intrusive (El-10, Wl-3), is steeply upturned and silicified near the intrusive contact and recrystallized throughout. Across the shallow, asymmetrical syncline to the east, the same section, but unmetamorphosed, is again exposed in the Mimbres fault in an arc about the intrusive. Several formations including the important Percha shale are sufficiently exposed to allow sampling for a three-dimensional study of the distribution of metals before and after contact metamorphism.

On Figure 1 in the unmetamorphosed eastern area near Georgetown, sections S1, S2, S3, and S4 are located in steep ravines under the cliff-forming Alamogordo member of the Mississippian Lake Valley limestone. The easily eroded Devonian section has been protected by this overlying massive limestone, leaving steep ravines cut in the shale (Fig. 4). By first removing the weathered surface of the rock, clean, fresh samples were obtained in the bottoms of the ravines. The aridity of the climate has prevented all but surface weathering of unfractured rock.

The metamorphosed sections are across very massive outcrops which were easily sampled after first removing about one-half inch of surface rock.

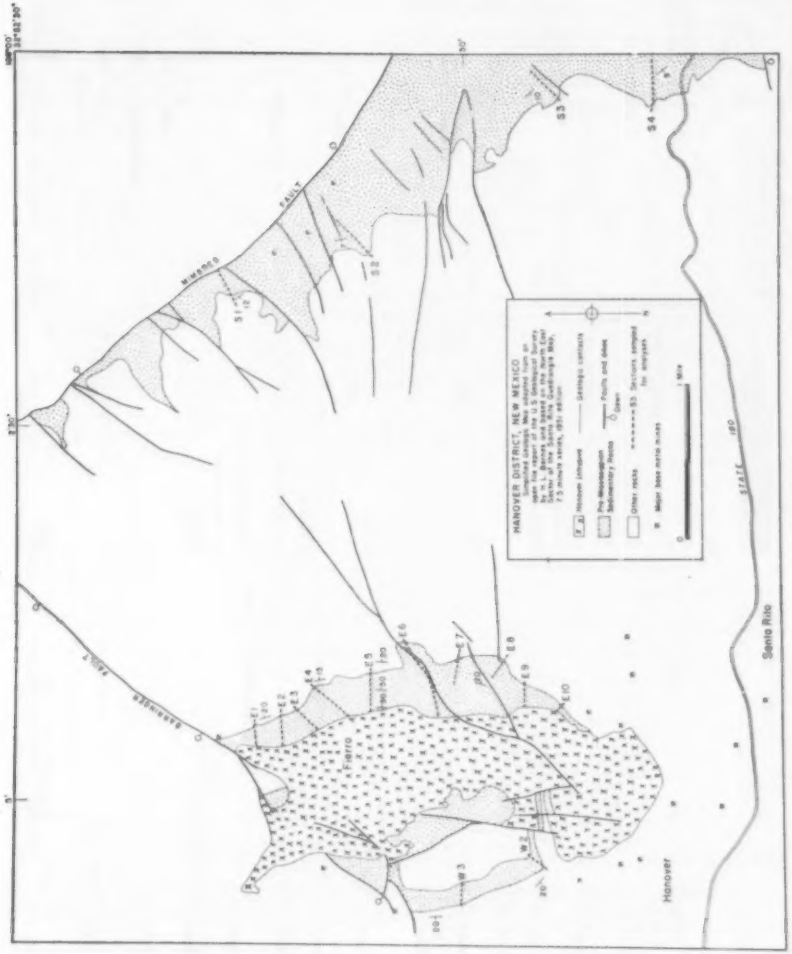
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FIG. 1.

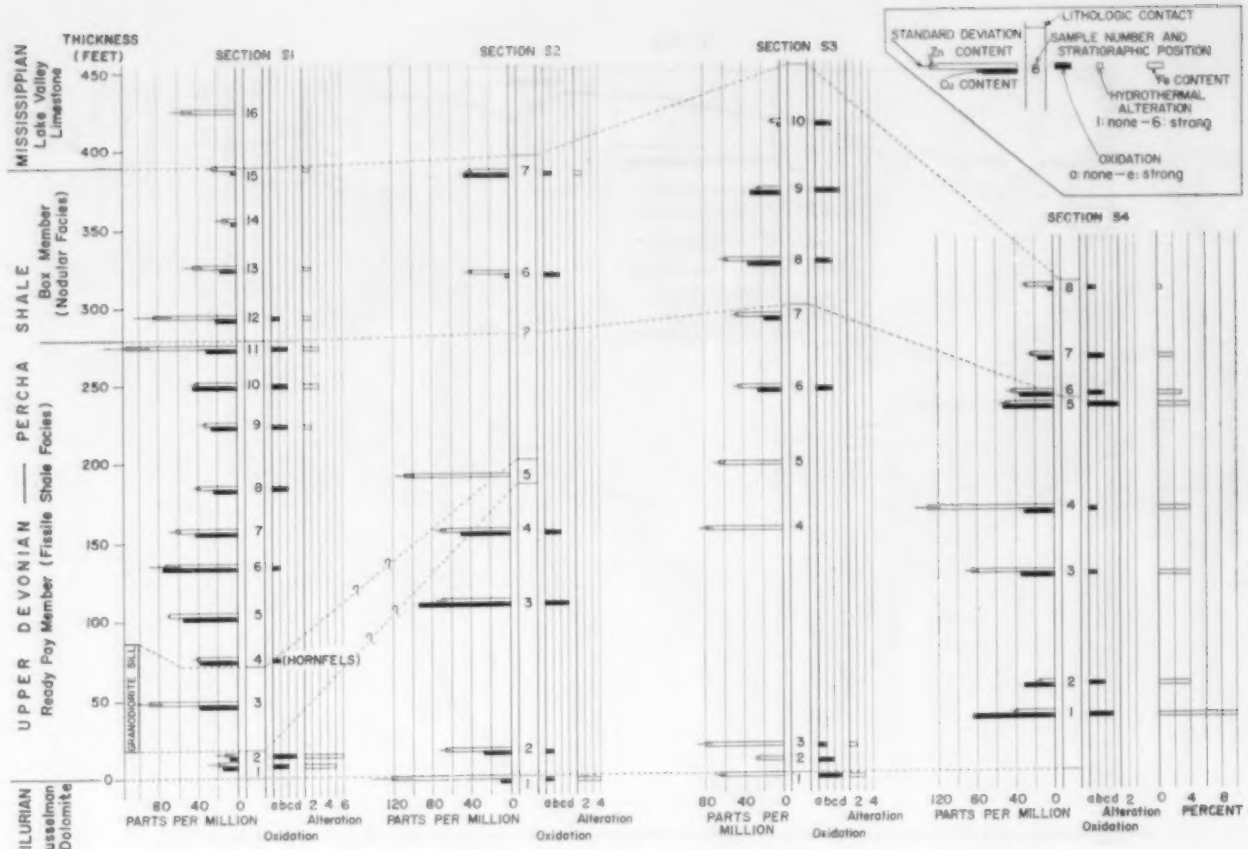


FIG. 2. Location and analyses of unmetamorphosed samples in the Hanover district.

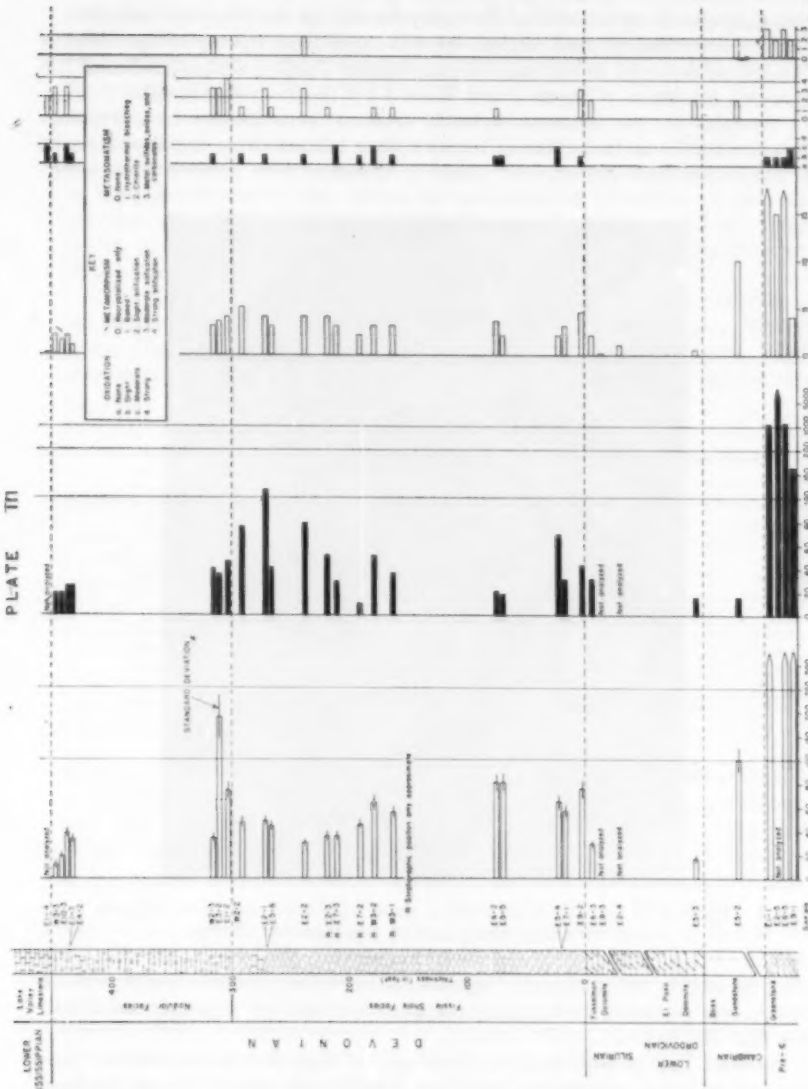


FIG. 3. Location and analyses of metamorphosed samples in the Hanover district.

These sections are located generally along ravines that drain from the surrounding metamorphic hills to the valley formed by the Hanover intrusive.

The unmetamorphosed sections were sampled from the top of the Silurian Fusselman dolomite to the basal Pennsylvanian Parting shale member of the Oswaldo formation. Figure 2 and Table 4 list the analytical results.

Samples on the unmetamorphosed sections were located by surveying. Samples on the metamorphosed sections were located either by measurement or estimation from the nearest contact. Although these sections were some-

FIG. 4. Contact of the Devonian Percha shale with overlying Mississippian Lake Valley limestone along section S1, Hanover district.

what thinned by being upturned against the intrusive, no correction was made because the distances to the nearest marker horizons are relatively small, i.e., less than 100 feet.

Schmitt (18, p. 804) has calculated on the basis of ore reserves and production, and rock and mineral analyses, that 600,000 metric tons of Zn have been added to the contact zone about the intrusive. Although no estimate of the probable error for this number was given, it is based on sufficient data to be more than adequate for the present calculation. To convert this number

to a more useful form here, if 100 ppm Zn were contributed by a 100-foot section of rock with a specific gravity of 2.6, then about 29 square miles of area are required to contribute this amount of zinc. Obviously the 18-foot thick Parting shale, the dolomites, or the limestones are insufficient as an appreciable source of Zn. The Percha shale cannot be dismissed on cursory inspection, however.

In order to evaluate the change in metal content of the Percha shale on metamorphism, it was necessary to locate the samples stratigraphically and to note independently the effects of oxidation or alteration on individual samples. Small sills were found to occur on sections S1 and S2 and faulting on S4, probably between samples S4-2 and S4-3, has affected the thicknesses of these sections and caused local alteration.

Sample Quality.—Samples were rated in the field in respect to oxidation by surface water on the basis of rust stains between shale layers, bleaching which pinched out in depth, and changes in mechanical strength. Hydrothermal alteration was also estimated on the basis of extent of argillic altera-

TABLE 4

ANALYSES OF THE UNMETAMORPHOSED MISSISSIPPIAN AND PENNSYLVANIAN FORMATIONS IN THE HANOVER DISTRICT

Formation	Sample	Cu (ppm)	Zn (ppm)
Pennsylvanian-Oswaldo formation			
Parting shale member, top	S1-21	116	86±15
Parting shale member, base	S1-20	110	124±20
Mississippian-Lake Valley formation			
Hanover limestone, top	S1-19	8	35±6
Hanover limestone, base	S2-9	17	12±3
Alamogordo limestone, top	S1-17	35	22±6
Alamogordo limestone, base	S1-16	0	55±12
Alamogordo limestone, base	S3-11	(less than 0.15% Fe)	

tion or by the size and frequency of calcite or quartz veins. When there was strong alteration or oxidation, it was very difficult to differentiate between the two effects, hence very few samples of this type were taken. The results of the estimation to separate roughly the effects of groundwater leaching or contamination and of hydrothermal alteration are given on Figures 2 and 3.

In the metamorphosed sections, it was necessary to discriminate between the contact metamorphism and local metasomatism where the metals might be erratically enriched. The skarn zone was either very narrow or absent along these sections and was not sampled; therefore, the extent of baking, silicification, and recrystallization gave a rapid indication of the extent of metamorphism. Metasomatism was avoided where possible but where unavoidable it was evaluated on the basis of the abundance of hydrothermal bleaching, chlorite, or the sulfides, oxides, or carbonates of the metals. Oxidation was estimated on essentially the same basis as for the unmetamorphosed sections.

Because the highest Zn content was to be expected in the fissile shale, the

averages of 55 ppm Cu and 70 ± 6 ppm Zn for 12 analyses of sample S1-5 had to be verified to see if they were representative of this sediment. The analyses of samples from the fissile shale, which showed no visible alteration and either no, or at most very slight (barely detectable megascopically) oxidation, gave averages of 41 ppm Cu and 69 ppm Zn. These results again show that Cu analyses tend to be slightly erratic and confirm that the Zn content of the Ready Pay fissile shale is 70 ± 2 ppm.

Summary of Unmetamorphosed Sections.—Several conclusions are evident from consideration of Figure 2. At any one horizon, after discounting oxidized and altered samples, there is little if any change within ± 10 ppm in primary Zn content over the approximately 3¼ miles sampled. This result could have been anticipated because there is little change in the described sections of Percha shale over large areas of New Mexico; therefore, it will be assumed that analyses of the unmetamorphosed sections are representative of the primary metal content of the metamorphosed sections.

There is little correlation between primary Zn, Cu, and Fe contents although each decreases vertically with increasing carbonate content of the Percha and Lake Valley formations. The poor correlation of the erratic variations in Zn and Cu content with oxidation and alteration emphasizes that geologic uncertainties are much greater than the analytical error. However, the fact that the analyses of the sill in S1-3 and S2-5 agree at 99 ppm within the analytical error suggests that here igneous rocks are considerably easier to sample than sediments.

Tentatively, there seems to be an enrichment of Zn at upper contacts which can be correlated with hydrothermal alteration, but what appears visually to be the same kind of alteration in S1-1 and S1-2 seems to have the opposite effect on metal content. More detailed study is necessary to make valid conclusions concerning this complex problem.

Summary of Metamorphic Sections.—The analyses on each metamorphic section have been projected onto one summary section (Fig. 3) based on the thicknesses on section S3. The fairly regular change in metal content vertically and the agreement between samples collected at the same horizon lends support to the accuracy of sampling and analyses on these sections.

By comparing analyses of samples approximately at the same horizon, it is apparent that Cu and Fe tend to be more mobile during silicification than Zn, which, in this shale, is more uniform in primary distribution. Due to the higher solubility of Zn compounds and its expected higher mobility, this conclusion is surprising. As a corollary, it might be pointed out that Cu and Fe have a tendency to follow each other in minor variations caused by oxidation, metamorphism, or metasomatism. The Precambrian rocks exposed are highly metasomatized adjacent to the intrusive and the reliability of the sampling for the analyses quoted may be in doubt although all megascopic metallic minerals were assiduously avoided in taking samples.

Change of Metal Content on Metamorphism.—For purposes of comparison on Figure 5 (and in disagreement with the maximum thickness of 315 feet quoted by Hernon et al. (9)), the total Percha shale thickness taken from

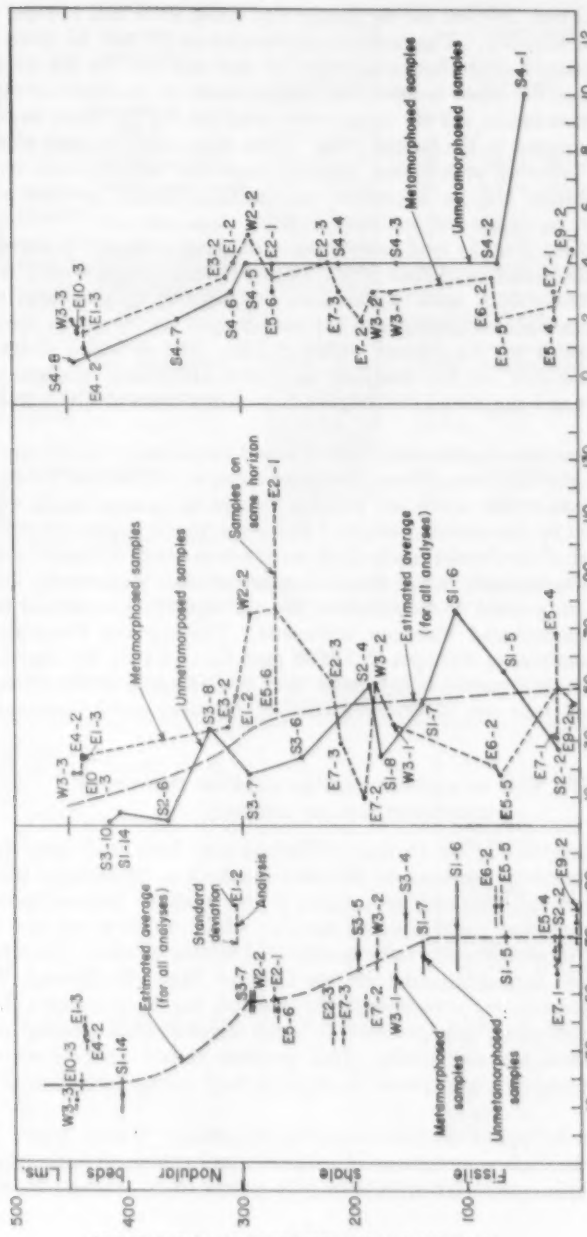


FIG. 5. Comparison of Zn, Cu and Fe content in metamorphosed and unmetamorphosed Percha shale, Hanover district. For location and interpretation of samples, see text. The apparent erratic variation in the copper content is caused by the difficulty of collecting representative samples.

section S3 is 452 feet, 299 feet for the Ready Pay fissile shale and 153 feet for the nodular Box Member. The positions of samples on S1 and S2 were adjusted proportionately after eliminating sills; S4 was not used for the Zn and Cu curves because the exact location and displacement of the fault or faults could not be determined. All S4 values were used for the Fe curve because the values are constant in the faulted area. Only those samples were plotted which met the following restrictions: unmetamorphosed samples with no or very slight oxidation and no alteration; and metamorphosed samples with none to moderate oxidation and no metasomatism.

Both Cu and Fe (Fig. 5) tend to increase in the limy shale and to decrease in the fissile shale on metamorphism which appears to have caused homogenization near the contact. In spite of this local mobilization, it is evident that within the Percha shale metamorphism has not changed the Zn or Cu content within $\pm$ 20 ppm or the Fe content within $\pm$ 1%. The difficulty of taking representative samples for Cu analyses, as noted previously, explains the erratic Cu curve and the actual distribution is probably close to the *estimated* average line.

It has been calculated previously that it would be necessary to derive 100 ppm Zn from a 100-foot section over 29 square miles to provide the Zn added to the contact zone. The maximum possible change of 20 ppm which might have been caused by the metamorphism of this shale would require derivation from the 300 feet of the Percha fissile shale section over about 50 square miles, yet the area of the intrusive is less than 2.5 square miles. Apparently, therefore, no significant portion of the metals in the ore deposits was derived from the nearby metamorphosed Paleozoic sediments. The exposed Precambrian rocks, which contain over 500 ppm Zn, 1,000 ppm Cu and 15% Fe, may have contributed to these deposits, but, because they are adjacent to the intrusive and altered, they may not be representative of the unexposed basement in the area.

ZN, CU, AND FE DISTRIBUTION IN PART OF THE UPPER MISSISSIPPI VALLEY DISTRICT

General Description of the District.—There is very little shale underlying the Zn-Pb ore-bearing limestone or dolomite horizons in Mississippi Valley districts, and there has been only very slight, if any, evidence (dolomitization) for metamorphism that could liberate metals. Metal sulfides are not sufficiently soluble in groundwater to be transported in this manner. Nevertheless, samples have been analyzed from the Calumet Mine, Shullsburg, Wisconsin, as a representative area in order to establish the metal content of the shales and to determine any gradient of metal concentration passing from the ore bodies into the wall rocks. This gradient should indicate whether wall rocks were enriched or depleted in metal content during formation of the ore deposit.

This deposit is typical of districts of the Mississippi Valley type. The ore is localized in shallow structures as sphalerite and galena, or both, replacing and filling open spaces but with very little galena in this mine. Faulting

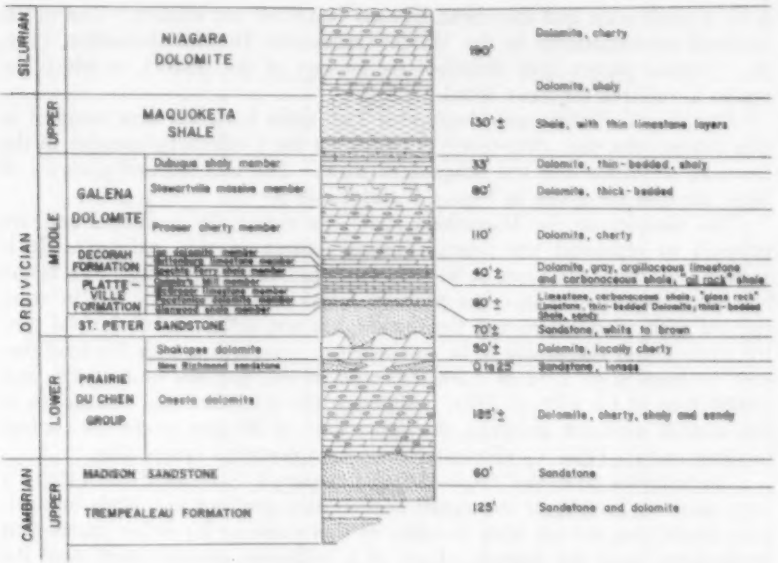


FIG. 6. Generalized columnar section of the Upper Mississippi Valley district (from Behre, Heyl, and McKnight (4)).

TABLE 5

LOCATIONS AND ANALYSES OF SAMPLES FROM THE MAQUOKETA SHALE, UPPER MISSISSIPPI VALLEY

Approximate stratigraphic distance above base (feet)	Sample number	Zn (ppm)	Cu (ppm)	Fe (%)	Geographic location
130	—	—	—	—	Top of bed
65	M-6	9	48	3	1 mile S. of Mill Creek Bridge on Highway U. S. 52, Peosta, Iowa quadrangle
?	M-5	21	79	3	2.5 miles N. of Highway U. S. 20 on road to Graf, Peosta, Iowa quadrangle
21	M-11	34	66	4	0.5 mile W. along Illinois Central R. R. from Scales Mound Station, Galena, Illinois quadrangle
21	M-12	37	50	3	390' W. of M-11
6	M-9	70	—	4	Same as M-11
6	M-10	31	75	3	260' W. of M-9
Average content		34	64	3	

is on a small scale and associated igneous rocks are not evident. The ore is localized predominantly in the Middle Ordovician Decorah formation (Fig. 6). Several papers have described the geology of this district, to which the reader is referred for more detail (1, 5, 10).

Sampling Locations and Analyses.—Two shale horizons were sampled in this district: the thin (five-foot) "oil rock" of the Guttenberg member of the Decorah formation and the Maquoketa shale. The location and analyses of these samples are given in Figure 7 and Table 5.

The samples of the Maquoketa shale are essentially unaltered and are believed to represent the primary metal content of this sediment. It is apparent that this shale cannot be a potential source for the metals now found in nearby deposits because the primary metal content is very low in comparison with other shales and the thickness is not sufficient for a metal contribution of this magnitude to be significant in comparison with the total district production to 1951 of 1,200,000 tons of Zn, 821,000 tons of Pb, and 10,000 tons of Cu (10, p. 232). Although the dolomites and limestones of this district were not analyzed, the upper limit of 20 ppm to the Zn content in these rocks (Table 1) eliminates them as a potential source also.

The samples from the Eagle-Picher Company's Calumet Mine (Fig. 7) were taken to investigate the metal concentration gradient in a shale immediately underlying the ore body in order to find evidence for either enrichment or depletion near the deposit. Lack of a minimum concentration near the deposit and the generally low level of the primary "oil rock" (about 20 ppm Zn, 60 ppm Cu, and 7% Fe) indicate that metal has been added to the shale even where mineralization is not evident. In these beds where dolomite and shale are interbedded with each a few inches thick, it was difficult to obtain representative samples; therefore, variation in sample quality explains the somewhat erratic results. It may be concluded that in this district, as in the Hanover district, the metal now in the ore deposits has not been derived from nearby Paleozoic sedimentary rocks.

ZN, CU, AND FE DISTRIBUTION IN PART OF THE PARRAL DISTRICT

General Description of the District.—The Parral district is located about 330 miles south of El Paso, Texas, in Chihuahua, Mexico, near the eastern edge of the post-ore volcanics of the Sierra Madre Occidental. The area of particular interest is the Frisco Mine of San Francisco Mines of Mexico, Limited, at the town of San Francisco del Oro about 14 miles west of Parral. The deposit consists primarily of a series of large veins with both open space filling and replacement common in a host rock of calcareous shale over 800 meters thick. A great many thrust faults and drag folds complicate the local structure. Top or bottom of the section has not been found, and there are no marker beds identified; therefore, the section is undated and correlations have not been made as any one bed can usually be followed only a few feet.

A skarn zone is found in the deeper parts of the vein, and intense silicification of the vein and wall rock forms an envelope about this skarn zone and in the upper parts of the vein, but the extent of silicification decreases rapidly

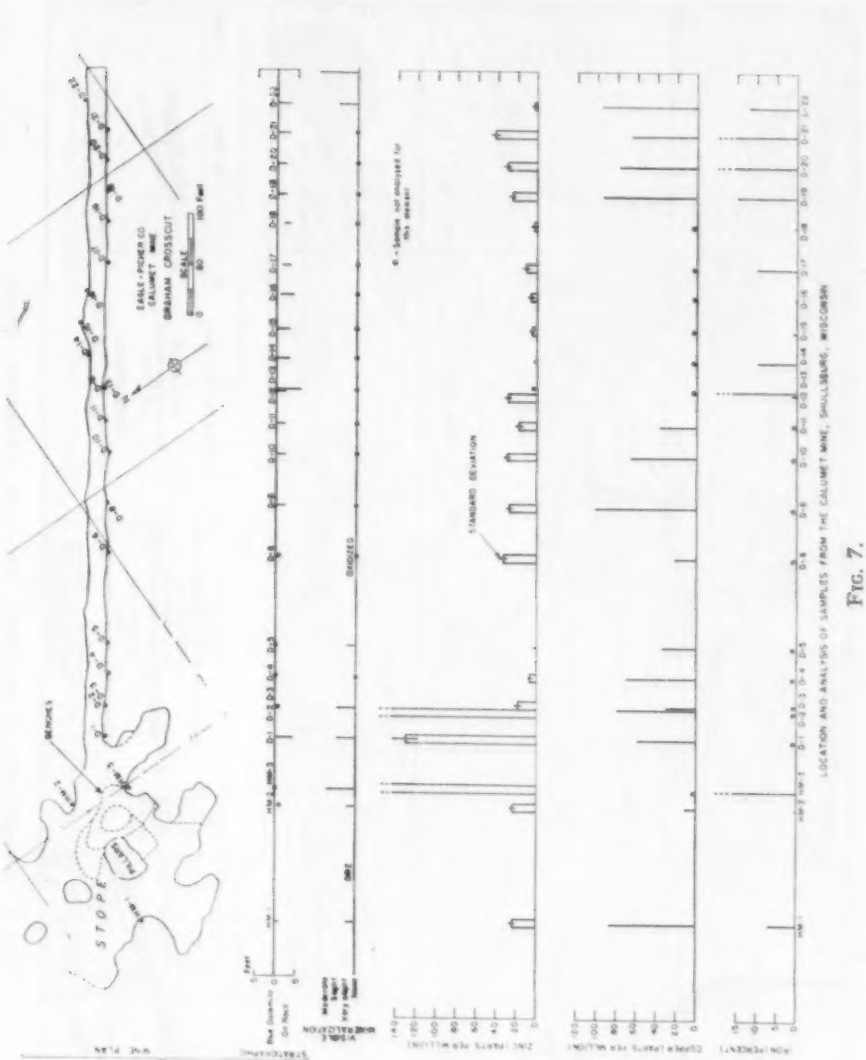

EARLE-FISHER CO.
CALUMET MINE
GRAHAM CROSSCUT
SCALE
100 Feet
STOPE
BEARINGS
STANDARD DEVIATION
LOCATION OF SAMPLES

FIG. 7.

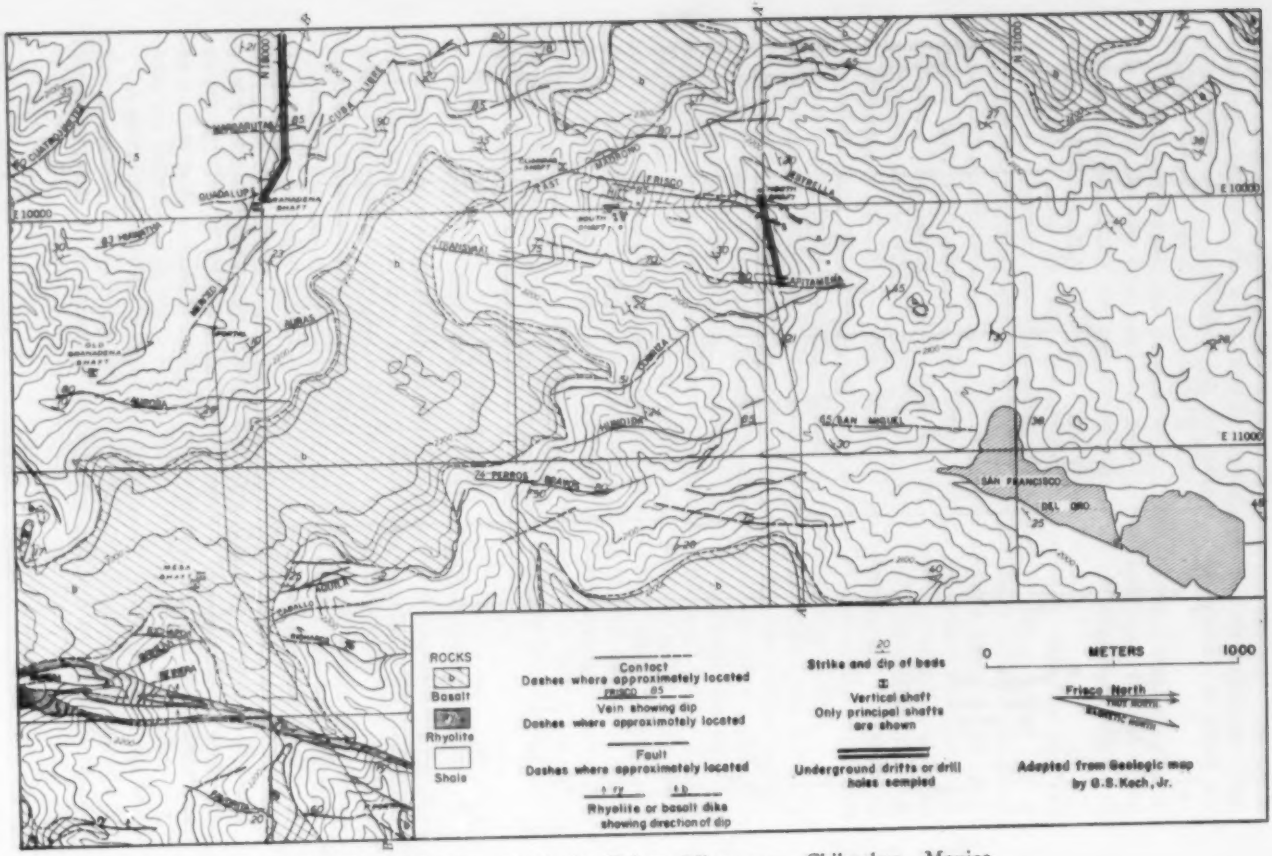


FIG. 8. Geologic map of the Frisco Mine area, Chihuahua, Mexico.

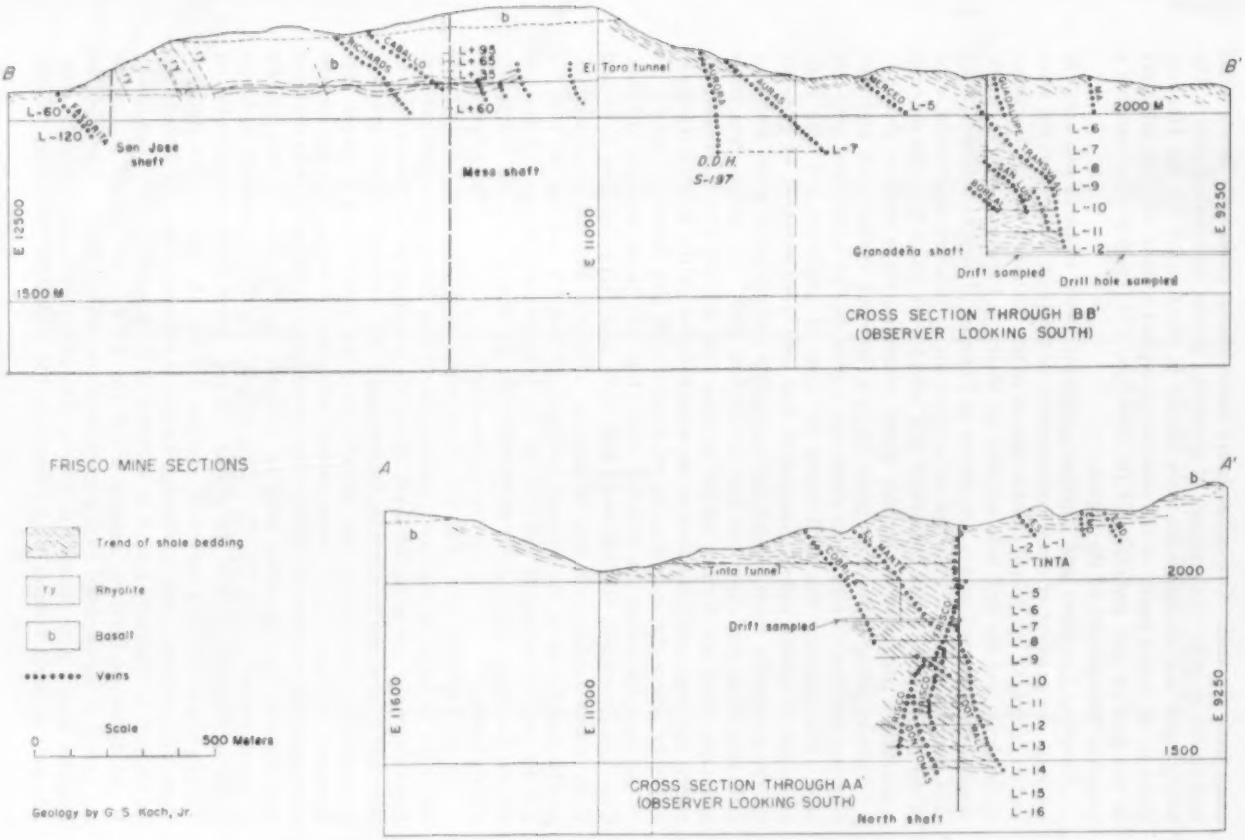

B
B'
b
El Toro tunnel
L+95
L+65
L+35
L+60
L-60
L-120
San Jose shaft
Mesa shaft
D.D.H. S-197
L-7
L-5
2000 M
L-6
L-7
L-8
L-9
L-10
L-11
L-12
Granadeña shaft
Drift sampled
Drill hole sampled
E 12500
E 11000
E 9250
1500 M
CROSS SECTION THROUGH BB'
(OBSERVER LOOKING SOUTH)
FRISCO MINE SECTIONS
Trend of shale bedding
Rhyolite
Basalt
Veins
Scale
0
500 Meters
Geology by G. S. Koch, Jr.
A
A'
Tinta tunnel
L-2 L-1
L-TINTA
2000
Drift sampled
L-5
L-6
L-7
L-8
L-9
L-10
L-11
L-12
L-13
L-14
L-15
L-16
1500
E 11600
E 11000
E 9250
CROSS SECTION THROUGH AA'
(OBSERVER LOOKING SOUTH)
North shaft

FIG. 9.

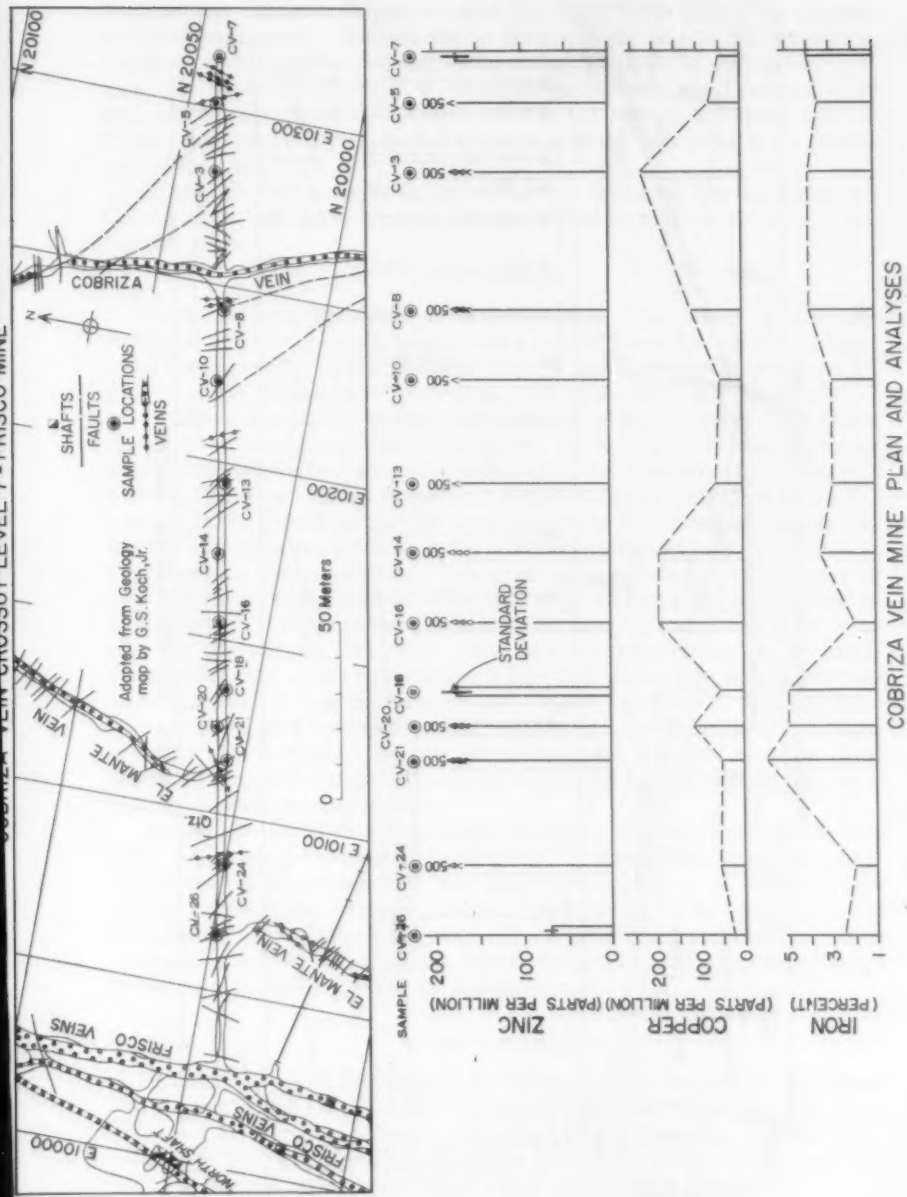
away from the vein. Ore minerals are found almost exclusively in the veins and consist in order of abundance of sphalerite, galena, and chalcopyrite. The ore, gangue and alteration are very similar to those noted for the Hanover district. A recent paper on the area sampled gives a more detailed summary of the geology and especially of the structure (11) and it also contains a complete bibliography of the region.

Sampling Locations and Analyses.—Samples were taken in two areas to establish the gradient of metal concentration in the shale away from the veins and to determine the primary metal content of the unaltered shale. Locations of the drifts and the drill hole sampled are shown in Figures 8 and 9. Locations of samples and assays are shown in Figures 10 and 11. The Cobriza vein samples are taken from one of the most highly silicified and veined areas of the Frisco Mine. The Transvaal vein samples are taken from the extreme northeastern portion of the district, where mineralization is weak or absent.

Samples along drifts were taken by first removing surface rock and then chipping one pint of rock from about one square foot of sulfide and vein-free area. All sampling was well below the zone of oxidation and was from areas free of sulfide veins. Samples of drill core were prepared by grinding off the potentially contaminated surface with a carborundum wheel and then collecting chips over about one foot of vein-free core. No attempt was made to sample along one horizon but the samples were selected free from contamination and over sufficient area to be representative of the bulk of the rock, especially where the shale was interlaminated with thin limestone beds.

All samples across the Cobriza vein (Fig. 10) were strongly silicified. The high Zn content falls off away from each vein except between C-14 and C-16, where another vein may be present. There is also, on these sections, greater enrichment in the footwall host rock of both Cu and Zn, but both Cu and Fe tend to be erratic and may be less homogenized during silicification. Fe, for example, seems to be enriched in the El Mante vein but not in the Cobriza vein.

In the Transvaal vein (Fig. 11) the gradient of silicification is more gradual in the footwall (to the east), and the Zn content follows the same pattern. Exploration for ore in the footwall, where the gradient can be followed for at least 200 meters, can be aided by Zn analyses. The regularity of this gradient is surprising, considering that samples were not taken along a single bed. Samples TE-2 and TE-13 were veined with, and of unusually high content of, respectively, calcite and quartz. In the hanging wall, Zn has been depleted near the vein in comparison with the 123 ppm Zn, 75 ppm Cu, and 5% Fe of the unaltered sample TV-25. This sample (TV-25) is believed to be an unaltered representative of the primary shale. Some pyrite disseminated on bedding plane surfaces occurs in samples TV-12, 18, and 25, but, because there is no evidence, such as veining, for sulfide metasomatism and because the Zn content is relatively low, it is assumed to be primary in the black shale. If the difference between samples TV-6 (or TV-8) and TV-25 represents the extent of Zn depleted during metamorphism, about 90 ppm Zn would be available from a zone possibly as wide as 100–150 meters adjacent to the vein. The vein is about 1 meter thick; therefore, the volumetric enrichment would



COBRIZA VEIN MINE PLAN AND ANALYSES

FIG. 10.

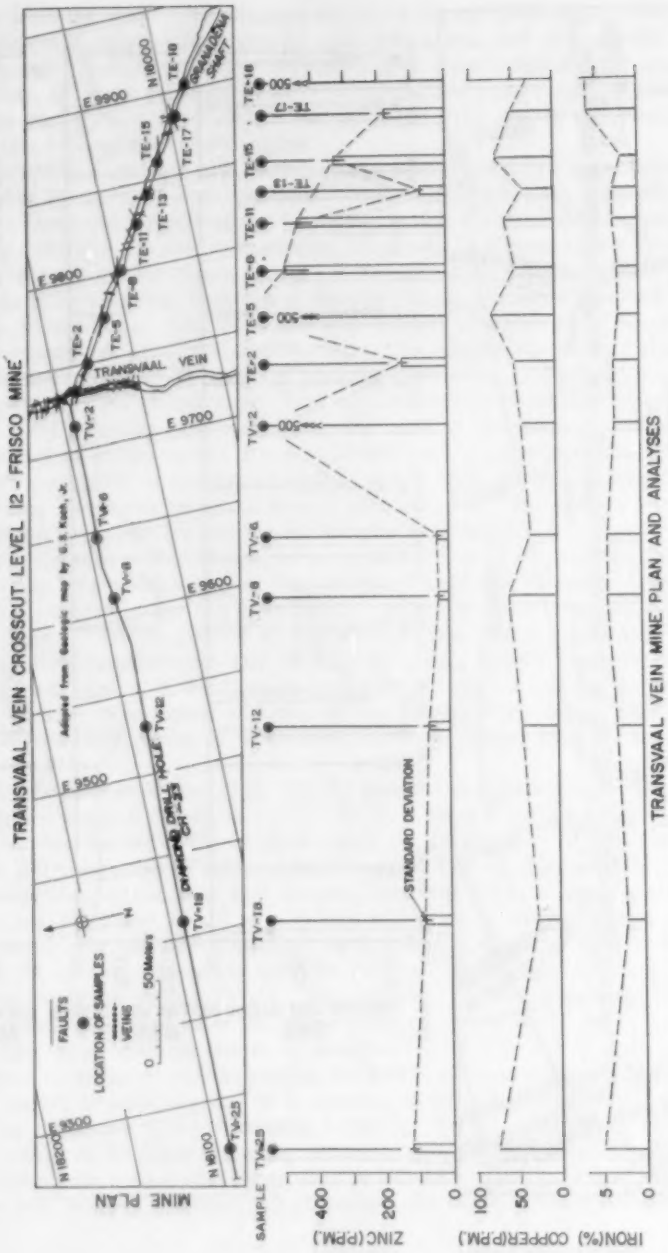

TRANSVAAL VEIN CROSSCUT LEVEL 12 - FRISCO MINE
MINE PLAN
Adapted from Geologic map by G.S. Koch, Jr.
TRANSVAAL VEIN
GRANODIORITE SILL?
DIAMOND DRILL HOLE CH-23
FAULTS
LOCATION OF SAMPLES
VEINS
50 Meters
N 18200
N 18000
N 18100
E 9900
E 9800
E 9700
E 9600
E 9500
E 9300
TE-1
TE-2
TE-5
TE-6
TE-11
TE-13
TE-15
TE-17
TE-18
TV-2
TV-6
TV-8
TV-12
TV-18
TV-22
TV-25
SAMPLE
ZINC (P.P.M.)
COPPER (P.P.M.)
IRON (%)
STANDARD DEVIATION
400
200
0
100
50
0
5
0
500
TRANSVAAL VEIN MINE PLAN AND ANALYSES

FIG. 11.

be about 100–150 times 90 ppm or about 1% Zn in the vein ignoring adjacent wall rock enrichment. Because the Zn content of the vein at this crosscut is nearly 4 percent and because that of the entire Cobriza vein drift is over 500 ppm, this amount is adjudged to be insufficient to form the Transvaal vein, and, furthermore, certainly can have contributed little to the metal content of the many veins and the adjacent enrichment in the wall rocks in the central part of the mine.

Cu and Fe tend to be as erratic across the Transvaal vein as across the Cobriza vein, with lower contents where silicified and higher contents in the primary shale.

CONCLUSIONS

On the basis of abundance of metals in rocks, black shales are the only sediments sufficiently rich in metals to be a potential source of metals for base-metal ore deposits. In the Hanover district, the change in Zn, Cu, and Fe content of the Percha fissile shale from contact metamorphism is insufficient to contribute appreciably to the metal content of the deposits. The shales of the upper Mississippi Valley district are too low in metal content for an appreciable contribution and the gradient of metal concentration in the wall rocks indicates enrichment rather than depletion during formation of the deposits. In the Parral district the metal content of the unaltered shale is also too low and again the gradient in the wall rocks indicates only very slight, if any, depletion from alteration. This gradient is sufficiently regular over at least 200 meters in the footwall of the vein to be used as a tool for exploration underground. The measured gradient in the hanging wall is too short to be used for this purpose, however. Thus, in a contact-metasomatic, a Mississippi Valley, and a vein type deposit, it has been shown that lateral secretion from Paleozoic or later sediments is not a significant process. Each of these districts is in an environment which, relative to other deposits of the same types, is rich in shales. Because lateral secretion does not occur in these seemingly propitious circumstances, it would not be expected in the same types of deposits in other districts.

It was also found that uncertainties in the evaluation of geologic factors (the extent of ground-water leaching or contamination, alteration, metasomatism, and metamorphism) and their variable effects on metal content greatly exceeded the errors in analysis. Reproducibility of sampling in the field had to be determined independently of analytical reproducibility. It is emphasized that this precaution is critical for geochemical sampling although it has been generally ignored in quoting errors.

ACKNOWLEDGMENTS

Without the aid of Professor C. H. Behre, Jr., and the facilities and financial support of the Ore Genesis Laboratory, Columbia University, this study could not have been undertaken. Professor Behre personally collected samples of the Maquoketa shale in the upper Mississippi Valley district and provided advice and encouragement for which the author is grateful.

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SCIENTIFIC COMMUNICATIONS

PENECONCORDANT URANIUM DEPOSIT—A PROPOSED TERM [1]

WARREN I. FINCH

The term peneconcordant is proposed to describe the form of the numerous and highly productive uranium deposits in sedimentary rocks of the Colorado Plateau, Wyoming, the Dakotas, and Texas. These deposits typically are tabular bodies nearly concordant (parallel) to the bedding of the host rocks. They differ from vein deposits in that they do not occupy or follow fractures or shear zones in the sedimentary rocks (10). Furthermore, they are not coextensive with a specific lithologic unit, such as uranium-bearing marine black shale.

The many terms now used to describe these uranium deposits are based variously on petrographic, mineralogic, geographic, and genetic considerations; none is satisfactory for describing all these deposits having a common and distinctive form. Furthermore, some of the terms are ambiguous and have been commonly used to group together deposits having distinctly different forms, such as uranium-bearing veins and uranium deposits nearly concordant to the bedding of the sedimentary rocks. Some of the terms previously applied to these deposits, in order of their presentation in the literature, are "sedimentary uranium deposits" (5, 7), "carnotite deposits" (5), "sandstone-type uranium deposits" (11, 13), "Plateau type uranium deposits" (1), "disseminated deposits in sandstone" (2), "bedded uranium deposits" under the general heading "concordant deposits" (12), and "epigenetic stratiform deposits" (8). Some of the above terms are not now applicable to these deposits because of (a) the general recognition of the epigenetic character of the uranium minerals and their young age compared to that of the host rock minerals (14), (b) the discovery of unoxidized equivalents of carnotite deposits, (c) the discovery of deposits of similar form in limestone and lignite, and (d) the discovery of similar deposits in numerous and large areas outside the Colorado Plateau.

These uranium deposits may have a common origin and may ultimately be placed within a genetic classification. However, the present divergence of views on their genesis precludes wide acceptance of any term that has genetic implications. Thus, it seems desirable to set apart these deposits descriptively rather than genetically by using a readily observable characteristic, namely their form.

The term proposed to designate those uranium deposits having a common

[1] Publication authorized by the Director, U. S. Geological Survey.

and distinctive form is *peneconcordant uranium deposit*. The word peneconcordant means "almost agreeing" (from the Latin *paene* and *concordans*, present participle of *concordare*), and in the geologic sense means almost conforming to or paralleling the bedding or other sedimentary structures of stratified rocks.

Peneconcordant uranium deposits are tabular, lenticular, or irregularly-shaped masses of widely differing size that are, in general, concordant to the gross sedimentary structures of the enclosing rock but that in detail cut across sedimentary structures. This local discordance is a diagnostic characteristic indicating that the deposits are epigenetic rather than syngenetic. The long dimension of peneconcordant uranium deposits is commonly oriented parallel or subparallel to sedimentary features, such as bedding, lenses, channels, and fossil logs. The long dimension is rarely, and then probably coincidentally, parallel or subparallel to tectonic structures, such as joints, faults, or shear zones.

The host rocks for peneconcordant uranium deposits are mainly arenaceous and argillaceous, and subordinately highly carbonaceous and carbonate rocks. The arenaceous and argillaceous rocks range from coarsely clastic—conglomerate, sandstone, and arkose—to finely clastic—siltstone, mudstone, and tuff. Small amounts of carbonaceous materials are common in the arenaceous and argillaceous rocks. Some host rocks are so highly carbonaceous as to be called lignites and coals. Carbonate host rocks are limestones that may be partly or completely clastic. The following outline gives examples of each class of host rock:

A. Arenaceous and argillaceous host rocks
   1. Triassic Chinle and Jurassic Morrison formations, Colorado Plateau region
   2. Tertiary formations, Wyoming and northern Colorado
   3. Cretaceous Inyan Kara group, Black Hills of South Dakota and Wyoming
   4. Eocene Jackson group, Texas Coastal Plains region
   5. Pennsylvanian Pottsville formation, Jim Thorpe (Mauch Chunk), Pennsylvania

B. Highly carbonaceous host rocks
   1. Tertiary Fort Union formation, Great Plains region of the Dakotas
   2. Cretaceous Dakota sandstone (for example, carbonaceous shale at the Hogback No. 4 mine), northwest New Mexico (6)

C. Carbonate host rocks
   1. Jurassic Todilto limestone, Grants district, New Mexico
   2. Jurassic Sundance formation, basal limestone, Mayoworth area, Wyoming.

The environment of deposition of these rocks was mainly fluvial and subordinately lacustrine, paludal, and marginal marine.

The uranium and associated minerals principally fill the original sedimentary and diagenetic pore spaces in medium- to coarse-grained host rocks.

These minerals, also, partially or wholly replace interstitial cement and detrital rock constituents, including plant remains and quartz grains. Replacement may predominate in carbonaceous, carbonate, and fine-grained clastic rocks. Much of the mineralized rock appears to be impregnated—a term expressing the irregular distribution of introduced mineral matter in a previously formed rock (9).

A few peneconcordant uranium deposits have uraninite or coffinite and iron and copper sulfides in microscopic fractures of rock mineral grains (4) and in minor macroscopic fractures in the host rocks (3). In such deposits the amount of mineral filling fractures is extremely small compared to that filling sedimentary and diagenetic openings. Furthermore, these fractures are not part of a prominent fault or shear zone. Oxidation and weathering of peneconcordant deposits very commonly redistributes some of the uranium and related metals in secondary minerals along joints, fractures, and faults as well as on outcrop surfaces and mine walls.

In conclusion, peneconcordant uranium deposit clearly sets apart a widespread and important type of uranium deposit that has a common and distinctive form, namely, nearly concordant to the bedding of the host rock. The meaning of the term is self-evident, and the term is readily applicable to field usage.

U. S. Geological Survey,
Denver, Colorado,
April 30, 1959

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Economic Geology
Vol. 54, 1959, pp. 947–956

DISCUSSIONS

THE WHITE PINE COPPER DEPOSIT

Sir: The White Pine copper deposit described by White and Wright in ECONOMIC GEOLOGY (Vol. 49, p. 675, 1954) has one feature in common with the sedimentary bed copper ores of Mansfeld Basin, Germany, and the ores of the Northern Rhodesia district in Africa, namely, sulfide copper dissemination in definite stratigraphic horizons. For the Mansfeld and Rhodesian deposits this feature coupled with the assumed absence of granite or other igneous rock from which magmatic ore solutions could have been derived, have led some geologists to believe them to be of syngenetic origin.

The White Pine ore body is composed of alternating layers of mineralized shales and sandstones, occupying an over all thickness of twenty-five feet or more. White and Wright advance the theory that the mineralized shale is of syngenetic origin, but that the sandstone copper was deposited from hydrothermal solutions and, therefore, is considered by them to be of epigenetic origin. Although a large body of quartz-porphyry occurs within a few miles of the mine area, the authors fail to mention it as a possible source for the sandstone copper.

Leaving aside, for the moment, the problem of an "out of sight" source for the copper, there remain only the field facts described in the article upon which the reader might independently arrive at a theory of origin for the White Pine ores.

The White Pine Fault.—One cannot fail to be impressed by the part played by the White Pine fault. Every plan map submitted in the article indicates a close relationship areally between the fault fissure and the ore distribution. Figure 11, p. 707, in particular, shows a fanning out of sandstone copper mineralization toward the southeast from the fault between the Old White Pine mine and the SE corner of Section 9. The authors make note of this fact and because of it they apparently feel compelled to subscribe to the theory that this sandstone copper was brought in by hydrothermal solutions moving up the fault fissure. However, in spite of their accepted theory of a hydrothermal origin for the sandstone copper, they cling to the hypothesis that the copper in the shale layers is of syngenetic origin, that is, deposited in water contemporaneously with the particles of sediment forming the original mud or shale. Thus, their theory for the White Pine deposits demands that the ore zone contains copper of two different ages; (1) the shale ore deposited in late Keweenawan times; and (2) ore deposited in the sandstones from hydrothermal solutions of post-White Pine fault age. The time gap separating the two periods of mineralization must have been very long indeed.

This very interesting theory involving two widely separated ages of copper mineralization in the same ore body seems to be worth discussing in some detail.

On the theory that the copper of the shale beds is of Keweenawan age, its areal distribution should show no relation to the later White Pine fault. If, however, the shale ore originally extended southwesterly to and beyond the position of the fault there should be a lower faulted extension of it to the southwest, that is, if the vertical throw is downward to the west.

There appears to be some uncertainty about the direction of throw and the amount of displacement along the White Pine fissure. The statement is made that "the horizontal component of slip along the fault would amount to over a mile, and the vertical component may not be more than a few hundred feet." With a lateral displacement of a mile, indicated on the map, the authors pre-fault age shale ore body must have been faulted to the position of the outcrop of the ore shales horizon in the extreme northeastern part of Section 6, long before the appearance of hydrothermal solutions in the fault fissure. With a horizontal displacement of less than a mile there should be a segment of shale ore down faulted opposite the White Pine mine area.

According to the authors, earlier scattered drilling southwest of the White Pine fault indicated only slight evidence of mineralization in the None Such bed. I am advised by Ira Joralemon (oral communication), however, that it is stated in U.S.G.S. Professional Paper 144 that good copper mineralization exists in the down thrown None Such formation, but from these results no information is available to this writer as to the copper minerals or their distribution in the shale and sandstone layers within the ore bed. The very important fact having some bearing on the respective theories of origin, is whether the grade of ore decreases away from the White Pine fault as it does northeasterly from the fault in the White Pine mine.

Furthermore, if there existed only the Keweenawan age shale ore with no superimposed later mineralization, drag shale ore should be easily recognized as such, not only in the White Pine fault but in other fault fissures of White Pine age where they intersect the shale ore bed. But, under the theory of two periods of mineralization, age relationships of individual copper minerals of the ore beds or of those depositional in and along the fissures might be difficult to determine. Yet, with two widely separated time periods of copper ore deposition, one marked by shale and the other by sandstone, as visualized by the authors, it should be possible both in the field and laboratory to distinguish the two ages of mineralization. Apparently no consideration of this phase of the problem had been given up to the time of publication. One may conclude that if there are no demonstrable differences in the kinds and space relationships of the copper minerals in the ores, this fact might well be considered as a strong argument in favor of a single period of ore deposition and an epigenetic origin for all the copper.

Distribution of Copper.—From the viewpoint of origin, the interpretations placed on the distribution of copper throughout the copper ore zone, Figure 8, could have much significance. Starting with the adopted theory of the authors that the copper in the sandstones was deposited from hydrothermal

solutions, it will be noted that every drill section shows no sandstone or shale section completely devoid of copper. This fact suggests one important thing, namely, that there was at the time of copper deposition in the sandstone a more or less complete copper-bearing water saturation of the 25 foot zone, including most, if not all, of the shale layers. However, solution travel was confined chiefly to the lower and upper sandstones, and in some degree to any relatively porous rock such as sandy shale, but there were also supplementary channels of limited solution travel, such as bedding planes and fractures, important enough at least to permit the ore solution to find its way into shales as well as in sandstone. This is confirmed by the authors, who say that "chalcocite and locally chalcopyrite occur as constituents of mineralized fissures," and, "films of native copper and chalcocite on joints are rather common in the parting shale in the drifts from the Schacht shaft."

The point has been raised against the epigenetic theory, and very properly too, that the White Pine ore shale is too hard and dense to permit the free passage of copper-bearing solutions. To this objection there is a good answer, which is, that the diffusion of metals into wall rocks outward from solution channels is being recognized as a phenomenon common to many ore deposits. All that seems necessary is that a part of the solution find its way into the rock to the point of saturation. There may be little or no movement of the water held in the rock but it serves as the medium through which diffusion from the moving solution takes place. The causes of deposition of the diffused metal, or metals, are in general little understood. At Butte, and in many other copper districts chalcopyrite, bornite, and pyrite disseminated in altered wall rock outward from veins is a very common feature. In these examples it is believed that the ore solutions spread into the rock as fast as it was altered, eventually reaching a point of saturation. Movement of the water of saturation is believed to have been extremely sluggish.

Causes of Copper Deposition.—What caused the diffused copper to be precipitated? This is a difficult problem common to most theories of ore deposition. In geological literature carbon is frequently mentioned as a probable ore mineral precipitant from hydrothermal solutions and it probably has application at White Pine. The better ore grades appear to correspond to higher carbon content in the shale layers immediately overlying the lower and upper sandstones. Also, it appears that the grades of sandstone ore may correspond to the distribution of carbonaceous material.

Source of Copper.—Thus it appears very probable that all the copper in the "copper zone" was brought there by the uprising hydrothermal solutions through the White Pine fault fissure. It is inconceivable that copper-bearing hydrothermal solutions could course through the copper zone without some of the copper diffusing into the shale and there be precipitated by carbonaceous matter, or by other agencies. Why not all of it? As to a probable source for the copper, consideration must be given to the presence of the large body of quartz-porphyry not far distant from the mine area. The parent magma of the porphyry was undoubtedly a much larger body of granite which may well be present at not excessive depths underlying the general area containing copper ores. The genetic association between quartz-porphyries, granites,

and copper ores, is not an uncommon phenomenon in the Western Hemisphere.

Native Copper and Chalcocite.—The authors report the presence of native copper associated with chalcocite in nearly all White Pine ore beds. A mill test indicates a ratio of 13 percent native to 87 percent chalcocite. In their consideration of ore genesis no mention is made of how the native copper might have originated, or from where. From any viewpoint of origin it would be of interest to know the spatial relation between grains and seams of chalcocite and native copper in the shale ore and whether, in the opinion of the authors, the simultaneous precipitation of chalcocite and native copper in the lagoon mud was chemically possible. The simplest and most logical explanation would seem to be that the native copper was the result of chemical reactions between the copper sulfide-bearing hydrothermal solution and the hematite in the sandstone. The ore deposit at Coro Coro, Bolivia, is a good example of an important native copper ore body formed through chemical reaction between a high copper-low sulfur ore solution and the hematite of a dark red sandstone. The ore zone containing disseminated native copper is bleached to a light gray color. Outward from the bleached area the red sandstone contains no copper. Native copper is the only copper mineral present. This writer suggests that at White Pine the presence of both native copper and chalcocite may have been the result of chemical reactions between a high copper-low sulfur hydrothermal solution and the carbon and hematite disseminated throughout the sandstone and shale layers composing the ore zone.

Epigenetic Theory.—Because of the fact that a hydrothermal solution from a deep seated source has been active in the deposition of copper and silver in the White Pine ore zone, the epigenetic theory may be properly called upon to explain many features of the ore occurrence, which seem inconsistent with the "source bed concept." The epigenetic theory would explain:

1. The fan-like spread of copper mineralization in the sandstones and the lower shale ore horizon in a northeasterly direction from the White Pine fault.
2. The irregular vertical range distribution of copper throughout the 25 foot "copper zone."
3. The presence of native copper and chalcocite in close association through the chemical reactions between a high copper-low sulfur and the hematite and carbon-bearing beds of the ore zone. Had there been excessive hematite with no carbon, as in the Coro Coro deposit, all of the White Pine copper would have been deposited in the native state.
4. The increase in ore grade of the sandstone and in the lowest but richest shale member as they approach the White Pine fault.
5. The relative abundance of copper in the high carbon "parting shale" compared to that in sandstone members. Sandstone grains of silica are probably not good agents of precipitation.

The epigenetic theory of origin would avoid the wholly untenable hypothesis of two widely separated time periods of mineralization during which the

same association of minerals, chalcocite and native copper, were deposited, syngenetically in the first period, and epigenetically in the second.

The challenge of the authors that there are barren intervening beds of shale between the upper and lower better grade ore layers is not entirely borne out by the drill hole assays in Figure 8. On the epigenetic theory the explanation of less carbonaceous precipitant in the lighter gray shales away from shoreline is certainly much simpler and possibly more understandable than any opposing theory of syngenetic origin which must involve climatic changes, alternating copper-bearing and copper-free sea or lake waters, crustal oscillations and erosional sequences, to say nothing of the whereabouts of the source rock for the copper; all of which present a problem too complex for solution by this writer.

Finally, from the descriptions of the geological and mineralogical relationships appearing in the text, supplemented by many plan and section maps, this writer finds much in support of a theory of epigenetic origin of the copper, but relatively little supporting the syngenetic theory for the shale ore proposed by the authors.

RENO H. SALES

BUTTE, MONTANA,
April 28, 1959

SOME GEOCHEMICAL CONSIDERATIONS ON LEAD-ISOTOPE DATING OF LEAD DEPOSITS

Sir: The recent publication by R. W. Boyle in this journal (vol. 54, p. 130–135, 1959) will cause grave misgivings concerning the interpretations of lead isotope variations. Some difficulties are mentioned that represent real uncertainties in any lead isotope study. However, in other cases the importance of the difficulties is exaggerated, and throughout the paper the discussion is presented in such a way to cast doubts on the whole subject in a way I believe to be unwarranted. I will confine my comments to the two sentences forming the conclusions of the paper; namely,

> "To conclude, I am of the opinion that fractionation of the lead isotopes takes place in geochemical processes, particularly in secretion processes. I would further stress that the lead isotope ratios recorded from deposits are the result of various geochemical processes through which the lead has passed, and that they are not, except in certain special cases, a function of the age of the deposit."

The reference to "fractionation" of lead isotopes is extremely misleading. According to common usage, isotopic fractionation is a process in which subtle differences in the properties of isotopes of the same element result in discrimination between the isotopes in physical and chemical processes. This effect for lead has never been observed in nature and is quite difficult to achieve by ordinary chemical manipulations in the laboratory. The process described by Dr. Boyle is not isotopic fractionation in this sense, but a separation of lead isotopes following the concentration of uranium, thorium and lead in different mineral species. This often leads to the production of radio-

genic lead from uranium and thorium in different minerals, and generally in different minerals from those in which primary lead is concentrated. As was pointed out in the paper under discussion, these different leads can suffer different histories during subsequent geochemical processes, particularly of the type considered by Dr. Boyle. Therefore the distinction between this process and true isotopic fractionation of lead isotopes may appear trivial; this is by no means the case. The different chemical affinities of uranium, thorium and lead have been well known for a long time and these have been widely discussed in interpretations of lead isotope ratios. Fractionation of lead isotopes in the usual sense is postulated to be insignificant and proof that this is not so would be a source of considerable embarrassment to the theories. The chances of this happening seem relatively remote.

The statement that the isotope ratios of lead are not a function of the age of the deposit is difficult to justify. A. O. Nier in 1941, first pointed out this correlation for the 25 lead samples then analyzed. Now eighteen years later, there are nearly 1,000 analyses available and the relationship has become more and more convincing. The only question is the precision of this relationship. A paper by the present writer and others in the Transaction of the American Geophysical Union, 1954, suggested uncertainties as high as 800 million years. Recent work indicates that this was pessimistic. The earliest papers on this subject recognized the importance of the geochemical processes described by Dr. Boyle and it has always been realized that they will result in a loss in resolution in ages obtained by lead isotope analyses. Despite the considerable effort that has been applied looking for these effects in nature, they have only been found in relatively rare instances in the case of a few extraordinary mineral deposits. It is for this reason that many of us have come to the conclusion that such surface processes as those described by Dr. Boyle are representative of only a short part of the lifetime of most lead samples and are not the major causes of lead isotope variations.

Apart from these considerations, the paper being discussed implies that the isotopic analyses of leads are generally used to indicate the age of lead deposits. This is not the case. The age value calculated from single lead isotope analyses usually refers to the time at which the lead was separated from its source rock; that is, the rock in which it existed since the formation of the earth at a time 4,500 million years ago. The relationships between this time of separation from the source rock and the age of ultimate deposition of the lead mineral may pose a very difficult geological question. It is only in the cases where intensive studies have been made and where a considerable mass of data has been gathered that the results can be properly interpreted in terms of age and history of the deposit itself. Even then the results are usually interpreted in conjunction with known geological relationships.

I would like to emphasize that the detailed geochemical considerations are of importance in interpreting lead isotope ratios, that their effects are much less than has been suggested by Dr. Boyle and that they have been considered in much more detail than would appear from his paper (see, for example, Nuclear Processes in Geological Settings, publication 400 National Academy of Sciences, U.S.A., and R. L. Stanton and R. D. Russell "Anomalous Leads

and the Emplacement of Lead Sulphide Ores," THIS JOURNAL, in press). I believe that these isotopic studies have already demonstrated their value and that their continued study will reveal important information of a geochemical nature about the outermost parts of the earth, and about the history and age of sulfide ore deposits.

R. D. RUSSELL

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VANCOUVER 8, B. C.,
May 2, 1959

THE SOURCE BED CONCEPT MOUNT ISA—EPIGENETIC OR SYNGENETIC

Sir: Several statements in B. P. Walpoles (ECON. GEOL., v. 53, no. 7, Nov. 1958, p. 890–893) vigorous but somewhat random letter are in need of qualification.

After remarking that "a considerable number of metalliferous geologists have had little practical training in the fundamentals of sedimentation," he states with respect to Mount Isa "Blanchard and Hall did not recognize that most of the crenulations and breccias described by them are in fact magnificent examples of primary slump structure." Elsewhere he criticizes Blanchard and Hall's ideas that the Mount Isa deposit is of epigenetic origin and says, "the syngenetic theory as applied to this particular deposit at least has the virtue of obviating the major problems inherent in any explanation of magmatic origin."

In general Walpole is intolerant of evidence "derived from a few polished sections" and of authors using the term replacement without knowing the details thereof. He prefers to rely on evidence accumulated by much regional and detailed mapping.

We do not concede that Mount Isa crenulations and breccias are examples of primary slump structures. The possibility has been considered by Mount Isa geologists, past and present, but no evidence can be found in the field to support the idea. The orebodies occur within shales at a distance of only a little more than 1,000 feet from a major overthrust fault. All major structural features within the mine area can be directly attributed to the drag effects produced by this fault. The various folds, crenulations, shears and breccia zones are all products of the same stress and probably are expressions of the differing physical properties of the shale horizons. The views of Knight (4) and Carter (5) concur with the folding being post depositional.

Bedding dips at 65°W and strikes approximately north–south. The axial planes of major and minor folds, the breccia zones and shears all strike a little west of north and dip 80–85°W. Thus the fold axes transgress the bedding planes. Some of the major folds show evidence of rupture along the axial planes of the synclines with the consequent production of shear zones and even faults with displacements of several hundred feet. The interrelation of the various structural features and their obvious association with tectonic stress rules out slumping as a major feature.

What might excite the attention of a sedimentary geologist are some of the minor crenulations. These, being quite spectacular and particularly "photogenic," have been often used as illustrations in published papers on Mount Isa geology and have on previous occasions led other geologists to suggest slumping. Significantly, however, the crenulations only exhibit any random orientation of axial planes when occurring within highly mineralized beds. Elsewhere they are consistently uniform and fit in well with the general structural picture. The former type, along with other minor features, can possibly be best explained by assuming a limited movement of the ore, under pressure, as a semi-plastic, highly viscous mass just prior to final consolidation.

The possibility of a syngenetic origin for the orebodies has not been overlooked at Mount Isa. Walpole is possibly not aware that the idea was first considered—and rejected—more than 20 years ago. Grondijs and Schouten (1) studied a suite of 250 polished sections and stated "a syngenetic origin of the ore is excluded and an origin by metasomatic replacement is proposed." Blanchard and Hall (2) in a supplementary paper concurred with these views and gave reasons therefor.

Subsequent advances in knowledge of geological processes along with exploration and development at Mount Isa itself has called for a reappraisal of these reasons from time to time. The basic principles of syngenetic deposition of ore have influenced field exploration by Mount Isa Mines Limited in various parts of Australia for the past several years. Applied to the Mount Isa deposits, however, it still fails to explain several major features of the mine geology.

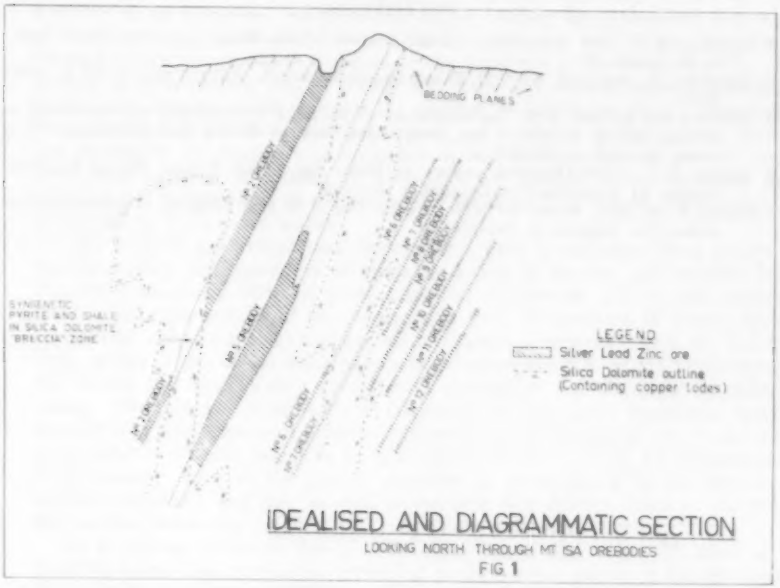
Walpole is dissatisfied with a metasomatic replacement origin for Mount Isa lead-zinc ore. Although an inspection of photo micrographs in the paper by Grondijs and Schouten (1) and O'Malley and McGhie (3) will show ample evidence of the replacement of shales by sulfide minerals, it is not necessary to rely on that as evidence for an epigenetic origin. Detailed underground mapping indicates that room is provided for the sulfides without removal of any significant amount of shale (5).

Possibly owing to a lack of detailed knowledge of the mine geology, he has also failed to mention the larger copper orebodies. These occur within a wide zone of shearing that trends across the shale bedding at an acute angle and in doing so, transgresses every one of the lead-bearing horizons. Some of these horizons carry lead ore on both sides of the shear zone, but within it they are totally devoid of lead-zinc mineralization. The shear zone has been silicified and dolomitized and chalcopyrite, sparse or otherwise, is distributed throughout its length. It is difficult to explain this segregation within a common stratigraphic column (Fig. 1).

Walpole is worried about the banding in Mount Isa ore. Banding is not an uncommon feature in other mines, and at Mount Isa it reflects the planes of structural weakness in the shale. The ore is notorious for its "slabbing off" behavior during mining operations. He also cannot "conceive . . . the means whereby the magmatic juices travelled from source to orebody." However, he states that fluids will tend to move towards the zone of low potential

energy and "perhaps syngenetically derived sulfides might do the same." May we ask why magmatically (or migmatically) derived sulfide minerals or sulfides and gangue minerals from deep seated metamorphic processes may not do likewise. Even the syngeneticists must face up to the fact that sparse syngenetic sulfides must move at least a limited distance to form ore concentrations. If a movement of two feet is possible, so is a movement of 10,000 feet.

Strangely enough, one of the most valid objections to a syngenetic origin for the ores lies in fine grained first generation pyrite. This is commonly accepted now to be syngenetic. This possibility was covered in the Grondijs and Schouten paper and recent research at Mount Isa has furnished evidence to support the idea. If the remaining ores are syngenetic then collector and


BEDDING PLANES
SYNGENETIC PYRITE AND SHALE IN SILICA DOLOMITE BRECCIA ZONE
LEGEND
Silver Lead Zinc ore
Silica Dolomite outline (Containing copper lodes)
IDEALISED AND DIAGRAMMATIC SECTION
LOOKING NORTH THROUGH MT ISA OREBODIES
FIG. 1

transport mechanisms must be assumed to account for their present location and structures. As these other ores contain considerable coarse grained pyrite, then it has to be explained how one lot of pyrite has been mobilized, yet the more obviously syngenetic pyrite still remains as isolated submicroscopic crystals with no evidence of alteration of their peculiar crystal structure or of any tendency towards migration.

At this time it cannot be established satisfactorily whether the ore is syngenetic with the shale, or whether it was syngenetic elsewhere in the shales and epigenetic to its present location, or whether it is of magmatic (or migmatic) origin. There is positive and negative evidence for and against

the complete acceptance to each of these possible modes of origin, and the most important problem at Mount Isa is the relationship of the copper deposits to the lead-zinc deposits.

Mr. Walpole has picked a poor example in trying to fit the unique Mount Isa deposit to his theories.

W. J. Murray and S. R. Carter

Mount Isa,
Queensland
and
Graham Hall,
Rosebery,
Tasmania,
March 26, 1959

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REVIEWS

Bauxites, Their Mineralogy and Genesis. Chief Editor: N. M. STRACHOV; Editor: G. I. BUSHINSKY. Pp. 488; figs. and tables. Moscow, 1958. Price, roubles 29.85 (only in Russian).

This is a symposium of 26 papers devoted to various aspects of the mineralogy, geochemistry, geology and especially the problem of the origin of bauxites, based upon Soviet experience and investigation of deposits occurring within the vast territory of the U.S.S.R. As mentioned in the Preface the symposium is a result of the work of a meeting of Russian bauxite geologists held at the Division of Geological and Geographical Sciences of the Academy of Sciences in 1955. The purpose of this meeting was to review and assess the present state of knowledge on bauxite deposits and to delineate the guiding principles for future prospecting. Intensified search for aluminum ores carried out in Russia in the last two decades has resulted in the discovery of a number of new bauxite deposits most of which have been explored in detail. A great deal of specific information has been gathered and certain ideas on the origin of these deposits advanced, which might be of interest to the western world.

The work is subdivided into three parts. Part I embraces three papers on the mineralogy and genesis of minerals occurring in bauxite and bauxitic clays. Part II is concerned with the general questions of bauxite genesis and comprises the five principal articles of the volume, and Part III contains 18 papers dealing specifically with the geology and genesis of individual deposits within the U.S.S.R. Only in five or six of the main papers is reference made to western literature on the subject and consideration given to the correlation and discussion of differing views. The volume closes with a resolution of the above mentioned meeting containing a brief statement of the results achieved in the last 20 years, as well as an account of essential points to be followed in the course of future investigations. Unfortunately, none of the papers presented is accompanied by an abstract or author's summary, and this, as well as the lack of a subject index at the end of the volume makes the usage of the symposium somewhat tedious.

In a general review of this kind it is possible to deal only with some of the essential points and conclusions arrived at in the various papers of the symposium. It has to be noted first of all that although most of the Russian geologists favor the theory of sedimentary origin of bauxite there are still great differences of opinion among many authors on various aspects of bauxite formation and throughout the volume strong controversies are apparent.

In Part I, in an article entitled "Mineralogy of Sedimentary Bauxites," pp. 7–50, S. I. Beneslavsky provides a useful discourse on all the minerals encountered in bauxite. The author points out that of the alumina minerals, diaspore is of secondary origin, but its presence in bauxite is not always an evidence of metamorphism of the deposits as is usually assumed. Under natural conditions alumina polyhydrates are converted into monohydrates (boehmite, diaspore), generally without the effects of high temperature. Boehmite is essentially an initial product of the crystallization of alumina-silicate gels, constituting the main part of the

original sediment. Gibbsite is found in bauxite in two forms: amorphous or cryptocrystalline (gibbsitic coagel) and crystalline; the occurrence of secondary stringers of coarsely crystalline gibbsite is a common feature of gibbisitic bauxites.

Kaolinite, the main carrier of silica in bauxite, is commonly found intergrown with diaspore and gibbsite, and is to be regarded as a mineral of the original sediment. Secondary kaolinite, resulting from resilification, is associated mainly with stringers and geodes in the bauxite. Iron-oxide minerals are essential constituents of all bauxites and the Fe_2O_3 content of gibbistic bauxites is higher than that of monohydrate bauxites. Hematite is associated mainly with monohydrate, and goethite with trihydrate bauxites. Goethite is commonly an oxidation product of siderite. Magnetite in quantities of less than 5 percent occurs mainly in monohydrate bauxites. A constant feature of all bauxites is the very uniform and equally distributed titania content, the most common titanium minerals being ilmenite, rutile, anatase and titanomagnetite. The average TiO_2-content of bauxites of all types is 2.45 percent, that of diaspore-boehmite bauxites 1.87 percent, boehmite-gibbsite 2.31 percent and gibbsite bauxites 3.16 percent. The character and mode of occurrence of titania suggest that it has to be regarded as an original constituent of the initial bauxite substance and that titania has not been introduced as clastic material. It probably entered the sedimentation basins of bauxite in the form of colloidal solutions together with alumina, silica and iron oxides and was precipitated as gel. The crystallization of this gel-substance produced anatase, brookite and rutile, ilmenite and titanomagnetite. The alteration of ilmenite and titanomagnetite into anatase, brookite, rutile, sphene and leucoxene is essentially an hypergenetic process.

The P_2O_5 content of bauxites ranges from trace to 0.8 percent, the average being 0.4–0.6 percent. A rise to 16–28 percent is exceptional in some of the deposits. The main phosphorus minerals of bauxite are apatite and vivianite, but P is also present in the form of ferruginous and aluminous phosphates. Phosphorus is also regarded as a part of the initial sediment precipitated from the solutions. The crystallization of the bauxite gel substance leads to differentiation and the formation of apatite and aluminum phosphate. Francolite, evansite and other phosphate minerals are secondary products. Some of the apatite of bauxites may also be of terrigen (clastic) origin.

In the closing section of his paper Beneslawsky stresses the importance of diagenetic processes in bauxite formation and gives in a tabular form (Table 18, p. 47) a useful genetic classification of bauxite minerals. Resilification due to the introduction of silica after the formation of bauxite is in Beneslawsky's view a process of little importance.

The role of diagenesis, epigenesis and metamorphism in bauxite formation is much more strongly emphasized by K. F. Terentyeva ("On the Genesis of Alumina Minerals in Bauxite," pp. 51–69). According to her, gibbsite (hydrargillite) is the primary mineral formed by crystallization of the alumina gel of the sediment, and gibbsitic bauxites occur only in those deposits that have not undergone a long epigenesis and have not been subjected to metamorphism. These are as a rule surface deposits that have remained uncovered since their formation, or deposits buried beneath a relatively thin sedimentary cover. More prolonged epigenesis leads to the formation of boehmite, which generally occurs in more deeply buried or dynamically affected deposits with dip angles between 25° and 30°. The origin of diaspore involves dynamic metamorphism, and the majority of diaspore bauxite deposits are associated with strongly folded or faulted wall rocks with dips of 70° to 80° or even vertical. Experimental data indicate that diaspore is

formed under pressure of over 1,500 kg/cm² and temperatures above 240°. The appearance in bauxite of a number of new minerals such as chlorite, micas, calcite, pyrite etc. is a result of hydrothermal metamorphism, while the formation of corundum and the conversion of bauxite into emery is performed by partial or total crystallization and dehydration at high temperatures (pyrometamorphism).

A. K. Sharova and A. K. Gladkovsky ("Mineral Composition, Origin and Alteration of L. Cretaceous Bauxites, Eastern Slope of Ural and Turgai Plains," pp. 70–79) find that the pellets of these bauxites are pebbles and differ in their mineralogical composition from the cement. They consist of less hydrated alumina minerals, α-magnetite and maghemite, and the cement is composed of Al-polyhydrates, hematite and hydrohematite. The authors are inclined to regard these bauxites not as chemical but as mechanical sediments reworked from some primary plateau-type lateritic deposits. The cement is regarded as derived from colloidal solutions. Subsequent weathering leads to the kaolinization of the bauxite and some redistribution of ore substance. In some deposits (Sokolov) the latter process has resulted in the formation of an epigenetic hydrated phosphate of Sr, Ca, and Al, a new mineral described by the authors as sokolovite with the general formula $2(Sr, Ca)O \cdot 4\ Al_2O_3 \cdot P_2O_5 \cdot 11\ H_2O$. Heating curves and refraction index determinations carried out by the authors on alumina minerals suggest that the hitherto accepted concept of the transition of gibbsite into diaspore or boehmite and further into corundum is not factual.

In the introductory article of Part II, G. I. Bushinsky reviews "The Theory of A. D. Archangelsky on the Genesis of Bauxite in the Light of Recent Data" (pp. 83–92). This theory, first advanced in 1933, and amended in 1937, has been very popular among Russian geologists, and in its various modifications is still the most widely accepted view, which has largely stimulated prospecting work, resulting in the discovery of a number of new deposits. It postulates the sedimentary-chemical origin of bauxite and suggests that aluminum and iron compounds are transported from the weathering areas in the form of molecular or colloidal solutions and are precipitated either in limnic-swampy depositional basins, or in marine lagoons mainly as alumina-ferric gels. Organic matter acts as an important stabilizer of solutions and leads to the formation of lignite or coal seams, which commonly accompany deposits of bauxite and bauxitic clays. In proposing this theory, the laterite theory, or residual formation of bauxite by tropical weathering, was essentially rejected, as well as the possibility of mechanical (suspended) transport of bauxite substance as suggested by Malyavkin and others. Also rejected was the terra rossa or limestone residue theory favored for Mediterranean bauxite by many European authors. Bauxites associated with limestone are interpreted by Archangelsky as being of sedimentary marine origin, while those associated with sandy-clayey beds, commonly accompanied by lignite, are regarded as limnic-lacustrine or swamp deposits.

Referring to the value of this theory and its possibly wider application Bushinsky states (p. 90) "Significant work on the study of bauxites has also been carried out in foreign countries. In this connection it is interesting to note that more and more economic deposits, previously regarded as leteritic, are now found to be sedimentary, but with regard to the Mediterranean bauxite, the origin of which was explained by the terra rossa (= limestone residue, V.A.Z.) theory, no serious study favoring this theory has been published since the work of A. D. Archangelsky. Thus a great many new facts confirm the wide occurrence of sedimentary bauxites."

Notwithstanding its great success Archangelsky's theory appears to be not

without defects, and in particular the postulated marine origin of many bauxite deposits seems to be questionable. Discussing the theory Bushinsky quite rightly suggests the following two necessary modifications: 1) the acceptance of the role of mechanical processes in bauxite formation, and 2) the recognition of the red bauxites of North Ural type, associated with limestone, as terrestrial or terrestrial-freshwater deposits.

In a paper entitled "Principles of Distribution of Bauxite Deposits and the Conditions of their Formation" (pp. 93–119), J. K. Goretzky shows that the formation of bauxite can be followed throughout the whole geological history of the earth since the Late Proterozoic. It is possible that some of the corundum-bearing rocks associated with Early Proterozoic and Archean metamorphics represent metamorphosed bauxite. In some periods the formation of bauxite was more intense than in others. The oldest known deposits are the Late Proterozoic (Sinian) bauxites of Bokson, East Sayan Mountains. Bauxite-bearing beds are found in Cambrian carbonate rocks in the Far East, but no deposits are so far known in the Ordovician and Silurian. The periods of most intense bauxite formation were Devonian, Carboniferous, Cretaceous and Tertiary. The author distinguishes and delineates the following world zones and regions of bauxite formation (b.f.) of various ages (map, Fig. 1, p. 96):

1) Uralo-Siberian Region of Palaeozoic geosynclinal b.f.
2) Regions of Palaeozoic platform-type b.f.: I. China, II. North Europe, III. North America, IV, Africa, V. Siberia (conjectural).
3) Region of Jurassic and Triassic b.f.
4) Nordic Belt of Cretaceous and Tertiary platform-type b.f.
5) Southern or Gondwana Belt of platform-type Tertiary and Quaternary b.f.
6) Alpine Belt of Cretaceous and Tertiary geosynclinal b.f.
7) Pacific Belts of Upper Tertiary platform-type b.f.: I. Asian, II, American.

Morphological, structural and palaeogeographical factors governing the distribution of bauxite deposits within these regions are discussed. Diagrammatic type sections are given for the marginal deposits of platform-type and the geosynclinal deposits. Discussing the conditions of bauxite formation Goretzky strongly criticizes the eluvial (residual) laterite hypothesis and then elaborates on the evidence in favor of the sedimentary origin. A rather complicated process of bauxite formation in swamps under the conditions of tropical climate is suggested, whereby sulfuric acid weathering is considered a major agent affecting disintegration of aluminum silicates, the migration of alumina, silica, and part of the iron compounds, and their subsequent accumulation in swamp basins. This is followed by diagenesis and subsequent reworking of diagenetically altered bauxite substance resulting in its grading and the separation of pellets and other aggregates from the finely dispersed clayey or colloidal material.

In a lengthy article "On the Geochemistry of Al, Ti, Fe, and Si, under the Conditions of Sulphuric Acid Weathering," pp. 120–161, M. N. Jakovljeva communicates preliminary results of detailed field and experimental geochemical studies carried out on the sulfidic deposits of south Ural in 1952, and on an alum swamp in 1953. In the first case the sulfuric acid weathering takes place in the absence of organic matter while in the second instance the swamp biocomplex plays an important role. It is found that the weathering of basal rocks leads in the first case to the accumulation of Si and Ti in the weathering mantle and the enrichment of iron and aluminum sulfates in ground water. In the presence of appreciable amounts of organic matter (peat) the weathering process results in the

removal of Si and Ti into the ground water and the partial retaining of alumina in the weathering mantle by organic compounds.

F. G. Pasova ("On the Conditions of Bauxite Formation," pp. 162–175) gives a brief but useful account of the structural features (texture) of bauxites as indicators of conditions of formation. The following structural varieties of bauxite are distinguished: clayey variety, consisting of finely dispersed homogenic substance of aleurite and pelite grade; breccia-like variety composed of clastic aggregates of angular or slightly rounded shape interbedded in a cementing matrix. Occasionally the aggregates display gel or collomorph structure indicating colloidal processes of chemical precipitation. Pisolitic bauxites show a combination of two structural elements. Pisolites of concentric structure as well as gel structures often found in the matrix are indicative of colloidal and chemical processes, while the occurrence of angular fragments of aggregates and the presence of fine clastic material suggest reworking or resedimentation of the material. Fragments of pisolites incorporated into complex pisolites of a later origin are indications of several generations of them. The mottled tubular varieties are characterised by the presence of tubular channels coated by light-colored bauxite substance and cutting the darker ferruginous ground mass. This variety does not show any indication of mechanical action and gel structures are common in many parts. Thus the study of structural features leads to the recognition of chemical colloidal processes in some cases and mechanical processes in others.

Chemical analyses show that the matrix of pisolitic bauxites is much higher in kaolinite (with SiO_2 content of 26–32%) and the pisolites themselves carry no kaolinite or only a negligible amount. This is attributed to the redistribution of the substance in the course of diagenesis.

The paper by G. I. Bushinsky "On the Genetic Types of Bauxite," the main article of the symposium, pp. 176–263, provides a comprehensive survey of the bauxite problem considering also the results achieved outside the U.S.S.R. The bauxite deposits of the world are classified into three major genetic groups: lateritic or residual, sedimentary-continental, and sedimentary karstic or continental-marine. Before elaborating on these groups the author gives a useful summary of salient data on the geochemistry of bauxite, on the solution, transport and sedimentation of bauxite components in sub-aerial conditions. Due attention is paid to the classical as well as to the latest researches on laterites and lateritic bauxites of India and other countries outside the U.S.S.R. and their origin discussed. In Russia itself true laterites or laterite bauxites are less well known and only a few occurrences are described elsewhere in the symposium. The following genetic varieties are recognized: 1) residual; 2) illuvial (after Marbut) and 3) sedimentary—deluvial, eluvial, lacustrine and marine mechanical and partly chemical.

The majority of workers consider only the residual type as true laterite and regard sedimentary laterites as reworked or redeposited residuals subsequently more or less altered by weathering. Oolites, pisolites and cavernous structures may occur in all laterites but the admixture of pebbles, gravel and sand is a feature of sedimentary laterites only. A most conclusive proof for residual laterite is the retention of the texture (structure) of the parent rock. The illuvial or residual-metasomatic bauxites are a special case of laterites formed by the replacement of felspars, nepheline and other minerals by gibbsite. Examples of such bauxites are those occurring on the basaltic rocks of Seychelles, on norites of Sierra Leone, on nepheline syenites in Arkansas and in Brazil, and on epidiorite rocks in British Guiana.

The author describes more fully the sedimentary bauxites and makes a comparative study of the following three well known deposits: Arkansas, Jamaica-Haiti, and the Urals. In Arkansas, following mainly Gordon and Tracey (1952), four genetic types of bauxite are distinguished: residual, colluvial, sedimentary bedded and conglomeratic. The relationship of sedimentary to residual deposits is here clearly demonstrated. The Jamaican deposits are the youngest representatives of geosynclinal karst bauxites, derived most probably from the lateritic weathering products of tuffs and andesitic rocks transported by intermittent karst waters and trapped in karst depressions in the Tertiary limestone (Zans, 1953, et seq.). The Devonian red bauxites of Urals being of similar nature and also associated with karstified limestones, are their ancient equivalents as are the Mesozoic and Palaeogene red bauxites of central and southern Europe and Turkey, carboniferous bauxites of central Asia and other deposits associated with limestone.

Following a detailed description of the Ural deposits, the author gives a brief history of the development of ideas of their origin. This is indeed an illuminating chapter, showing the great diversity of opinion, from the terra rossa theory applied in 1931 when the Ural bauxites were discovered, through a widely held belief in their marine origin and the recent return to the continental ideas. A number of earlier theories have been abandoned as invalid, for instance the biochemical theory of L. S. Berg, while others are still lively discussed. On the terra rossa, originally thought to be the residue of limestone solution, Bushinsky says "It has been shown now that the terra rossa of limestones in typical areas (Yugoslavia, N. Italy) consists of hydromicas with the admixture of iron oxides and kaolinite, while minerals of free alumina are absent, so that it has nothing to do with bauxite" (p. 256).

Bushinsky's own interpretation of the genesis of the Ural bauxites is briefly as follows. Red bauxites constituting the lower and greater part of these deposits are of continental origin. These are unfossiliferous and accumulated in the same manner as the Jamaican deposits contemporaneously with karst development. Intermittent streams inundating karst depressions deposited their suspended load derived from nearby areas of lateritic weathering of aluminum silicate rocks. Circulating warm ground waters brought about the decomposition of aluminum silicates into free alumina, removed carbonates and silica, leaving behind oxides of Fe, Ti, and Al. Thus the process of lateritization, commenced in the weathering mantle, continued and was completed in karst pockets. The grey bauxites forming the upper part of the deposits and carrying marine fossils, are essentially chloritized products of resedimentation of the red bauxite formed at the beginning of a later marine transgression, which subsequently led to the deposition of overlying thick limestone beds. Geosynclinal conditions provide a favorable background for such a process of bauxite formation since the basal aluminum silicate rocks in such areas are often found exposed at higher elevations than the limestones on which the lateritic waste products tend to accumulate.

Bushinsky ends his article with a brief discussion of the main criteria in prospecting for bauxite subdividing such criteria in two groups—climatic and geological.

The first two papers of Part III are devoted to bauxite deposits of Bokson (N. S. Iljina, "Geology and Genesis of Bokson Bauxites, E. Sayans," pp. 267–281, and P. V. Orlova, "Lithology, Conditions of Formation and Distribution of Bauxite in Bokson Deposits, pp. 282–305). These are the oldest known bauxites of Sinian to Lower Cambrian age, associated with dolomites and occurring under

rather complex structural conditions. The ore is slightly metamorphosed and consists of diaspore, boehmite, hematite and clay minerals of the kaolinite group, plus some mica and chlorite. Due to the high silica content it is of low grade. Its chromium and nickel content is indicative of basic or ultra basic source rocks. Marine or lagoonal sedimentary origin is contemplated although there seems to be sufficient evidence of their being formed during a continental break in marine sedimentation at the end of the Proterozoic.

Marine origin is also ascribed to the Devonian bauxites of Salair Range associated with the unevenly denuded surface of reef limestone (M. P. Nagorsky, "Genesis of Devonian Bauxites of Salair Range," (pp. 306–318). Of much theoretical interest is the study by K. N. Trubina on the "Ancient Lateritic Weathering Mantle in the Area of the North Onega Bauxite Deposits," pp. 319–334. Two lateritic horizons of Upper Devonian to Lower Carboniferous age discovered by drilling in the south-east marginal belt of the Baltic Shield are described, one developed on Proterozoic diabase porphyrites and another on Devonian mottled clays. The latter may well be the deluvial derivative of the former. The weathering mantle of diabase-porphyrites consists of 3 zones (in ascending order): micaceous-montmorillonite zone of about 5 m in thickness; kaolinite zone, 5.4 m, and the ferruginous-gibbsitic zone, 7 m.

The same author, K. N. Trubina, gives a brief description of "Bauxite-bearing Deposits of the Sub-Moscow Basin," pp. 335–346. On the southern flank of this basin bauxite-bearing beds are found filling karst depressions in Lower Carboniferous limestone and are overlaid by coal-bearing clayey beds. They represent a mixture of clay minerals (allophane, kaolinite, halloysite) with gibbsite of a poor quality. They carry in places a rich pollen and spore flora of Lower Carboniferous age. Sedimentary origin is evident and sulfuric acid is thought to be the leaching agent. Marine-lagoonal sedimentary origin is ascribed to the low-grade bauxite deposits of Jurassic age occurring on karstified Triassic limestones near Rachov in Eastern Carpathians (A. A. Denisevitch, "Bauxites of the Carpathians and Their Genesis," pp. 347–350).

In a brief article on "Bauxites of S. Ukraine and Their Genesis," pp. 351–354, J. B. Bass finds that on the southern rim of the Ukrainian crystalline massif bauxites are associated with 1) the mottled weathering mantle of pre-Cambrian amphibolites and schists, and 2) the clayey sediments of Middle Eocene age. Both are gibbsitic with small amounts of boehmite. Bauxites of the first type are eluvial, while those of the second are sedimentary. The Middle Eocene bauxite-bearing deposits contain plant remains, spores, and tests of Gümbelina.

The following two papers, N. A. Karzchavin's "Lower Cretaceous Bauxites of the E. Slope of Urals and Their Genesis," pp. 355–360, and B. P. Krotov's "On the Genesis of the Lower Cretaceous Bauxite Deposits of Urals," pp. 361–377, are concerned with the origin of the Mesozoic bauxites in the region east of Urals. These are associated with and generally occur in the upper part of kaolinitic clays filling either large buried valleys cut into igneous and sedimentary rocks or karst depressions in limestone. The deposits are mainly gibbsitic commonly showing distinct clastic features (pisolitic pebbles etc.)

A detailed study of one such deposit (Sokolov) leads B. P. Krotov to the conclusion that they are of secondary deluvial origin and are nothing but detrital derivatives of an ancient lateritic weathering mantle of Devonian diabase porphyrites. In Lower Cretaceous times the debris of this mantle was transported into low-lying shallow basins where the deposits subsequently underwent diagenesis and were converted into bauxite. Krotov expresses the opinion that such deposits

are of much wider occurrences than previously thought. He thinks that of the U.S.S.R. deposits, the bauxite deposits of Tichvin and Nikopoljsk are of this type, as are some of the deposits of France, New Guinea and Arkansas. Fully recognizing the importance of terrestrial lateritic weathering and the deluvial origin, Krotov rejects Archangelsky's concept of the sedimentary-chemical origin of bauxite.

The next five papers are devoted to the bauxite deposits of Kazakhstan of which those of Amangeljdinsk in the north-central part of the country are the largest and are of economic importance. The various deposits of Kazakhstan range in age from Albian to Upper Oligocene and are mainly gibbsitic. Their sedimentary nature is apparent although views still differ as to their chemical or detrital deluvial origin. The majority of authors support the theory of chemical sedimentary origin. E. P. Boitzova, N. M. Michailov and N. K. Ovetshkin ("Geology and Bauxite Prospects of the SW Part of the Turgai Embayment," pp. 378–392) delineate some of the laterite areas, which in Albian and Santonian shortly before the major Upper Cretaceous marine transgression delivered material for these deposits accumulated in shallow limnic basins. The chemogen mode of origin is supported by A. N. Volkov in a very informative article, "Bauxites of Kazakhstan and Their Genesis," pp. 393–415, as well as by B. A. Tjurin in "Deposits of Gibbsitic Bauxite in the Ore District of Amangeljdinsk, Central Kazakhstan," pp. 416–430. N. A. Ljisicina ("On the Mode of Occurrence of Kainozoic Continental Bauxites in Western Kazak Highlands," pp. 431–439) analyzes the structural features of bauxite deposits of the region and their association with karst. The bauxite deposition in karst pockets is found to be contemporaneous with karst development, a view also held by A. N. Volkov.

Most of the bauxite-bearing beds of Kazaktstan carry a rich pollen and spore flora, and the quantitative pollen analysis has proved to be a valuable aid in the age determination as well as for ascertaining the climatic conditions prevailing during the bauxite sedimentation (B. N. Razumova, "Stratigraphical Position and the Age of Bauxites in the Upper Reaches of the River Ashi-Tasti-Turgai, Kazakhstan," pp. 440–450, and K. V. Bogoljepov, "On the Stratigraphical Position and Genesis of Bauxites of Jenisei Range," pp. 454–461).

In a brief note on the "Mottled Deposits of Salair Range," pp. 451–453, M. P. Nagorsky describes the occurrence of ferruginous bauxitic clays in an ancient weathering mantle (eluvial) as well as in sedimentary clay series of Mesozoic and Paleogene age. Irregular deposits of bauxitic clays commonly fill karst pockets. An interesting occurrence of bauxite in the form of boulders and pebbles in Quaternary deposits along the middle reaches of the Jenisei River is described by J. A. Lavrushin and E. N. Stchukina ("Contributions on Bauxite Occurrences of Jenisei Area," pp. 462–477). Pebbles of pisolitic bauxite up to 10 cm in diameter occur here abundantly in ancient terrace deposits indicating that they have not been transported far from the source. The source beds have not been found but are believed to occur in the vicinity where drill holes have revealed certain sandy bauxite-bearing beds in the Upper Cretaceous. Karst bauxites are also probable in the area recommended for further detailed prospecting.

The last article of the symposium is a brief note by L. P. Konnov on "Mesozoic Bauxites of Middle Asia," pp. 478–482 in which the author mentions that altogether about 90 deposits and occurrences of bauxite have been recently recorded in the Mesozoic of Middle Asia. Of these, however, only 14 carry bauxite of conditional grade and but few appear to be of economic importance. Deposits of Baisunsk, S. and N.E. Fergan and those of the Pskemsk Range are the most

important. They range in age from Upper Triassic to Cretaceous (?) and many of them are associated with karst. Konnov regards them as chemical, partly metacolloidal deposits formed in swampy or limbic basins.

Thus the symposium provides much factual geological information, particularly concerning the mode of occurrence of a great variety of bauxite deposits and occurrences in the U.S.S.R. ranging in age from late Proterozoic to late Tertiary. True lateritic bauxites derived from tropical weathering of aluminosilicate rocks in situ are recorded from the Onega district in th emarginal belt of the Baltic Shield, the southern parts of the Ukrainian crystalline massif and certain parts of the Asiatic U.S.S.R. Most of the bauxite deposits of Russia are, however, of sedimentary origin, deluvial, alluvial, or limnic-lacustrine.

As to the various theories on the actual mode of formation of sedimentary bauxites, it appears to the reviewer that the purely chemogen theory as advocated by Archangelsky and his followers is by no means proven. In particular, the concept of the marine origin of bauxite, still widely held by a number of Russian geologists, seems to be untenable. In fact all stratigraphical and palaeogeographical evidence, where available in sufficient detail, indicates conclusively that bauxite formation takes place during periods of prolonged continental breaks in marine sedimentation. A consideration of various articles from the symposium shows that most of the sedimentary bauxite deposits of the U.S.S.R. are associated with ancient karst features. Karst being an indisputable manifestation of subaerial weathering is one of the strongest proofs in favor of the terrestrial or subaerial mode of bauxite formation. Diagenesis of argillaceous sediments under conditions of tropical weathering is another important factor not to be overlooked. Consequently, the main guiding principle in prospecting for bauxite deposits should be the locating of continental breaks within a stratigraphical succession where tropical weathering and karst development have prevailed.

V. A. ZANS

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KINGSTON, JAMAICA, W. I.,
June 4, 1959

Die Niederrheinische Braunkohlenformation. Fortschritte in der Geoligie von Rheinland und Westfalen, heraugegeben vom Geologischen Landesamt Nordrhein-Westfalen. Vols. 1 and 2. Edited by R. TEICHMÜLLER and G. V.D. BRELIE. A symposium introduced by Wilhelm Ahrens representing fifty-six contributors. 764 pp., 61 plates, 244 figures, 36 tables, Geologische Landesamt Norrhein-Westfalen, Krefeld, Germany, 1958 (in German).

This voluminous symposium assembles in one binding, although representing two volumes, many of the results of investigations carried on through recent years of the lignite or brown-coal formations of the Lower Rhine Basin. It is recommended to the attention of those interested in the stratigraphic and structural problems of the geology of western Europe and in the nature, origin, constitution, and modifications of the brown-coal deposits in general or of this region in particular.

Volume 1 (384 pp.) concerns the Oligocene marine beds in the northern part of the Lower Rhine Basin and Volume 2 (380 pp.) deals with problems of the Oligocene and Miocene non-marine beds in the southern part of the basin. In Volume 1 there are three sections dealing successively with the Tertiary sedimentary profile, the sedimentation of the marine beds, and with the flora and

fauna of these beds. In Volume 2 there are 5 sections. Section 1 concerns the geophysical and paleogeographical survey of the southern part of the North Rhine Basin; Section 2 with Oligocene deposits; Section 3 concerns the principle coal beds; Section 4 discusses features of beds overlying the coal beds; and Section 5 is a summary of the present state of knowledge and of unsolved problems relating to the Lower Rhine Brown Coal Basin.

Only a general idea of the scope of the articles making up the symposium is provided by the 19 contributions making up the section on Sedimentation in the marine Oligocene in Volume 1. The subjects of these articles include a study in variations in grain size and porosity of the sediments, stratigraphic significance of such variations, analysis of Schlumberger logs, phenomena accompanying shaft sinking by freezing, glauconite occurrence in molding sands, heavy mineral profiles, uranium enrichment in the marine Oligocene, use of Ca/Mg relationship to establish the fact of marine influence, use of pollen fossils to indicate near strand line origin of a coal bed, "wash-out's" and quicksand intrusions of coal beds with interesting illustrations, a humus gel pipe in the roof sand above a coal bed, changes in thickness and facies characteristic of sediments lying between two adjacent beds, and the discovery of fossil magnolia wood in the marine Tertiary.

This section (Vol. 1 Sec. 2) contains the largest number of individual articles but a similar wide scope of interests is manifest throughout the publication. Undoubtedly of special interest to coal geologists will be M. Teichmüller and P. W. Thomson's article on facies types of brown coal deposition and M. Teichmüller's article along the same line containing large colored plates illustrating the three types of coal accumulations during the Tertiary, more or less based upon modern swamp types.

R. Teichmüller in the final section of the book summarizes the main problems of the brown-coal deposits under the four general headings of stratigraphy, structure, paleogeography and origin of the great thickness of the main coal beds.

GILBERT H. CADY

URBANA, ILLINOIS,
May 4, 1959

The Evolution of North America. By PHILIP B. KING. Pp. 190; figs. 96; maps. Princeton University Press, Princeton, N. Y. Price, $7.50.

This is a treatment of the evolution of North America, including newer information on geological, geophysical, and geochemical investigations. After a preliminary discussion on maps the author takes up the natural history of continents, their constitution, surface features, permanence, accretion, and continental drift. The following 8 sections are treatments of separate regions of the continent—Canadian Shield, Interior Lowlands, Appalachia, Lands and Seas South of the Continent, the Cordillera, Eastern Ranges and Plateaus, and Cenozoic rocks and structures of the Cordillera.

Each section covers the geologic history of the region, geosynclines, structural features, mountain building, stratigraphy, surface features, mineral deposits, igneous activity, growth of ideas and controversies, and early surveys. Each section includes extensive bibliographic references and is adequately illustrated with charts, drawings and beautiful sketches illustrating fundamental and special geologic features. Four end pages give the sources of the illustrations, and the index is unusually complete.

The reader is impressed with the amount of pertinent information included, with the tremendous reading and culling out of non-pertinent data involved, and with the excellent organization of the work.

The book is bound to become the leading reference work, and it should also prove to be an excellent textbook for courses on the geology of the United States and of North America.

The Chemistry and Physics of Clays and Other Ceramic Materials, 3rd ed. By ALFRED B. SEARLE and REX W. GRIMSHAW. Pp. 942; figs. 220. Interscience Publishers, Inc., New York, 1959. Price, $16.25.

In the twenty-five years that have elapsed since the second edition of this book appeared, the science of clays and clay minerals has been revolutionized. This book is an attempt to modernize the subject. So rapid are the advances in the subject that an edition even in five years would be out of date. The publications of the Annual Conference on Clays and Clay Minerals contains much new material in each annual volume. This 3rd edition requires all of its 942 pages to bring the subject up to date.

Its fourteen chapters are: The Nature of Clays and Other Ceramic Materials; Atomic and Crystalline Structure; Crystal Structure of the Silicates; The Crystal Structure of Non-Siliceous Ceramic Materials; The Identification and Estimation of Minerals in Ceramic Materials; The Chemical and Mineralogical Composition of Ceramic Raw Materials; Physical and Structural Properties of Raw Ceramic Materials; The Influence of Water in Ceramic Systems; Changes in the Physical State of Ceramic Materials Brought About by the Removal of Water; The Equilibrium State and Physico-Chemical Reactions; Chemical Changes in Ceramic Materials; Physical Changes in Ceramic Materials; Strength and Allied Properties; and Miscellaneous Properties of Ceramic Materials.

This up-to-date edition assembles in a single volume a great mass of data that will make it the convenient reference book on this subject.

Clays and Clay Minerals. Edited by ADA SWINEFORD. Proc. 6th National Conference on Clays and Clay Minerals at Berkeley, Calif., Aug., 1957. Pp. 348. Pergamon Press, New York, 1959. Price, $8.50.

This proceedings of the Sixth National Conference is more comprehensive than its predecessors. It consists of 42 papers and 5 abstracts, contributed by 44 authors.

There are three main groupings of papers. One group is devoted to the characteristics of clay mineralogy; another group to the physical chemistry of clays and clay suspensions; and a third group to progress of clay mineral research in six other countries. One paper by Charles Meyer and Julian Hemley deals with "Hydrothermal Alteration in Some Granodiorites," and another by W. M. Bundy and H. H. Murray is on "Argillization in the Cochitic Mining District, New Mexico." The various papers give the latest techniques in the study of clay minerals.

This volume is Monograph 2 of the new Earth Science Series whose editor-in-chief is Earl Ingerson. It presents the most comprehensive source of advances in clay mineralogy and will prove invaluable to students of clay mineralogy as a ready reference and textbook.

Basic Geology for Science and Engineering. By E. C. DAPPLES. Pp. 609; figs. 247. John Wiley & Sons, New York, 1959. Price $9.50.

The author has developed this work somewhat differently from most textbooks on physical geology. It is designed apparently, not as a text for the general student in geology, but for pre-professional students who plan to follow engineering and science. In each chapter he progresses from factual data to interpretations, theory, and generalizations. There are three broad units: earth materials, processes of erosion and deposition, and processes of crusted deformation and metamorphism.

First considered are soils viewed from a geological and engineering standpoint. Several tables and graphs relate to particle sizes. This is followed by physical and chemical properties of rock-forming materials, rock-forming minerals, and igneous rocks. Numerous graphs illustrate the classification of rocks. Next comes soil-forming processes, which include weathering. The succeeding chapters are streams, shoreline processes, ground water, wind deposits, glaciation, sedimentary rocks, crustal deformation, metamorphism, and tables for the determination of common minerals.

Graphs, tables, and charts are used abundantly for illustrative purposes. The chief emphasis is on the development of principles suitable for application rather than on descriptions of occurrences. Missing are the customary treatments of geologic time, land sculpturing, submarine geology, earthquakes, and the earth's interior.

The book provides a basic ground work in physical geology, particularly for civil and mining engineers, and hydrologists.

BOOKS RECEIVED

CYRUS W. FIELD AND JOHN E. COTTON

A Preliminary Inquiry into the Formulation and Applicability of the Geological Principle of Uniformity. C. H. CRICKMAY. Pp. 50; pls. 8. Price, $1.85. Evelyn de Mille Books, Calgary, Alberta, Canada. *A critical examination of the law of uniformity leads the author to conclude that its current usage is too rigid and must, therefore, include greater variations in causes and effects to be useful in solving current geologic problems.*

Geophysical Activity in 1958. COMMITTEE ON GEOPHYSICAL ACTIVITY OF THE SOCIETY OF EXPLORATION GEOPHYSICISTS. Pp. 18; figs. 10. *Total worldwide geophysical activity in 1958 was reduced 7.7 percent compared to the previous year.*

Engineering Geology Case Histories. No. 3, Symposium on Rock Mechanics. Pp. 76. JOINT AMER. SOC. CIVIL ENGINEERS AND GEOL. SOC. OF AMER. COMM. ON ENGINEERING GEOLOGY. Geol. Soc. America, May, 1959. Price, $1.00. *Four articles: Engineering Studies of Rock Movement in Niagara Area, by A. D. Hogg; Rock Mechanics in T. 1 Underground Power Station, Australia; Importance of Geological Information in Tunnel-Lining Design, by W. T. Moody; Effect of Elastic Properties on Rocks of Civil-Engineering Design, by W. J. Judd.*

Explanatory Text for Preliminary Geological Map of Connecticut, 1956. JOHN RODGERS, R. M. GATES, and J. L. ROSENFELD. Pp. 64; figs. 3; preliminary geological map of Connecticut. Connecticut Geological Survey Bull. 84, Storrs, 1959. *This text accompanies the new preliminary geological map of Connecticut compiled in April 1956.*

Compte Rendu Sommaire des Séances de la Société Géologique de France. Pp. 28; figs. 2. *Report of the 1959 sessions of the Geological Society of France.*

Sand Size Fractions of South-Peruvian Barchans and a Brief Review of the Genetic Grain Shape Function. G. C. AMSTUTZ and RAYMUNDO CHICO. Pp. 6; fig. 1. Reprinted from Bull. Ver. Schweizer. Petrol.-Geol. u. Ing., Vol. 24, No. 67, 1958. *Size analyses of sand from different parts of Peruvian dunes.*

Geology and Ground-Water Resources of Mitchell County, Kansas. W. G. HODSON. Pp. 132, pls. 9; figs. 17; tbls. 17. Kansas Geological Survey Bull. 140, Lawrence, 1959. *Geography, geology and ground-water resources of Mitchell County, north-central Kansas.*

1958 Oil and Gas Developments in Ohio. G. G. SHEARROW and T. A. DEBROSSE. Pp. 29; figs. 3; tbls. 14. Ohio Geological Survey Rept. of Investigations 37, Columbus, 1959. *The steady increase of crude oil and gas production since 1951 continued throughout 1958. Falling prices, however, lessened the increase in value of this additional production.*

Fodikwan Iron Deposits. M. L. KABESH, M. S. AFIA, and A. L. WIDATALLA. Pp. 24; figs. 16; tbls. 2. Republic of the Sudan Geological Survey Bull. 4, Khartoum, 1958. *A short geologic report on the origin and future development of the Fodikwan iron deposits, Dungunab District, North Eastern Red Sea Hills.*

Bureau of Mineral Resources, Geology, and Geophysics—Melbourne, Australia, 1958–1959.

Rept. 37. The Geology of the Coastal Area between the Lower Gascoyne and Murchison Rivers, Western Australia. M. C. KONECKI, J. M. DICKINS, and T. QUINLAN. Pp. 144; pls. 5; figs. 9; tbls. 4. *Comprehensive report on the geology and oil and ground-water potential of Paleozoic, Mesozoic, and Tertiary sediments along the coastal area of Western Australia.*

The Australian Mineral Industry—Quarterly Review and Quarterly Statistics. Vol. 11, No. 3. Pp. 18; tbls. 11. Price, 3/–. *The main increases in export revenue, during the decade may be expected from alumina, copper, lead, and zinc, and moderate increases from asbestos and coal.*

Bull. 54. New Aconeceratinae (Ammonoidea) from the Albian and Aptian of Australia. R. O. BRUNNSCHWEILER. Pp. 19; pl. 1; fig. 1. *Description of several species of Aconeceratinae occurring in the Windalia Radiolarite (Upper Aptian) of the Carnarvon Basin of Western Australia.*

California Division of Mines—San Francisco, 1958.

Bull. 177. Geology and Mineral Resources of Santa Ysabel Quadrangle San Diego County, California. RICHARD MERRIAM. Pp. 42, pls. 2; figs. 3; photos. 16. Price, $1.50. *Stratigraphy, structure, physiography, and economic geology of the Santa Ysabel Quadrangle. Geologic maps, scale 1:62,500, in pocket.*

Spec. Rept. 53. Igneous and Metamorphic Rocks Sequoia and Kings Canyon National Parks, California. D. C. ROSS. Pp. 24; pl. 1; figs. 3; photos 24; tbls. 2. Price, 75 cents. *Geologic map, scale 1:62,500.*

Illinois Geological Survey—Urbana, 1959.

Circ. 265. Barite in the Southern Illinois Fluorspar Districts. J. C. BRADBURY. Pp. 14; fig. 1; tbl. 1. *Perhaps several small commercial barite deposits may occur in the southern Illinois fluorspar district.*

Circ. 266. Water-Sorption Characteristics of Clay Minerals. W. A. WHITE and ERNESTO PICHLER. Pp. 20; figs. 21. *Results of an investigation to determine the water-sorption characteristics of clays and other mica minerals show that montmorillonite absorbs more water than kaolinite, illite, and chlorite.*

Circ. 269. Plastic Properties of Coal. E. D. PIERRON, O. W. REES, and G. L. CLARK. Pp. 36; pls. 4; figs. 7; tbls. 16. *A discussion of techniques and results from the investigation of plastic properties of coal. The plastic behavior of a fluid coal is shown to be destroyed by pyridine extraction.*

Cooperative Ground-Water Rept. 1. Preliminary Report on Ground-Water Resources of the Chicago Region, Illinois. MAX SUTER, R. E. BERGSTROM, H. F. SMITH, and others. *Initial report of a joint series of publications designed to present results of ground-water resource investigations carried on cooperatively by the State Water Survey and the State Geological Survey. This report indicates that glacial drift and shallow dolomite aquifers yield more than half of total ground water pumped from the region in 1957. The potential yield is considerably larger than present withdrawal. Map of glacial geology and cross-sectional map in pocket.*

Cooperative Ground-Water Rept. 1-S. Summary—Preliminary Report on Ground-Water Resources of the Chicago Region, Illinois. MAX SUTER, R. E. BERGSTROM, H. F. SMITH, and others. Pp. 18; figs. 4. *A brief summary of the geology and hydrology of the Chicago region.*

Geological Survey of Jamaica—Kingston, 1958.

Publ. 42. Geonotes: Quarterly Newsletter of the Jamaica Group of the Geologists' Association. Pp. 30. Price, 6/6d.

Publ. 41. Annual Report of the Geological Survey Department for the Year Ended 31st March, 1957. Pp. 20. Price, 2/–. *Reports covering geologic mapping, ground water data, topographic and cave surveys, and special investigations.*

Geological Survey of Japan—Hisamoto-cho, Kawasaki-shi, 1958–1959.

Geological map of Oita. Scale, 1:200,000 Compiled by KONROKU TSUSHIMA and KOJI ONO in 1957.

Geological map of Kochi. Scale, 1:200,000. Compiled by HIROSHI ISOMI in 1957.

Rept. 182.—Some Aspects of Multiple Geophone Setting and Pattern Shooting in Seismic Reflection Prospecting. TETSUICHI KANEKO. Pp. 60; figs. 67; tbls. 3. *Consideration of the theoretical relation between multiple geophone setting and pattern shooting. In Japanese; English abstract and summary.*

Bulletin—Vol. 10, No. 1. Pp. 74; pl. 1; figs. 55; tbls. 11. *Twelve papers: six deal with airborne radiometric regional surveys; six deal with regional radiometric surveys with car-mounted instruments. In Japanese; English abstracts.*

Institute of Geology and Paleontology Tohuku University—Sendai, Japan, 1959.

Number 49. Tertiary Orogenesis in Northeast Honshu, Japan. NOBU KITAMURA. Pp. 98; figs. 23; tbls. 10. *The Tertiary geologic history of Northeast Honshu is discussed with respect to four sedimentary provinces recognized with the region. In Japanese; English abstract.*

Miocene Diatom Assemblages from the Onnagawa Formation and Their Distribution in the Correlative Formations in Northeast Japan. TARO KANAYA. Pp. 130; pls. 15; figs. 6. *Sixty-four diatom forms were distinguished. They are*

distributed in twenty-three genera; and fifty species and varieties were identified, including eight new species. In English.

Province of Quebec Department of Mines—Quebec, 1959.

Geological Rept. 77. Madeleine River Area Electoral District of Gaspé-North. H. W. McGERRIGLE. Pp. 50; pls. 8. *General geologic report on the stratigraphy, structure, and economic geology of the Madeline River area. Geologic map, scale 1:63,360, in pocket.*

Outline of Progress of the Mining Industry in the Province of Quebec during the Year 1958. EDGAR-E. BÉRUBÉ. Pp. 10; pls. 5; fig. 1; tbl. 1. *The value of mineral production for Quebec decreased 12.2% from the 1957 level. However, mineral development and exploration showed a substantial increase over the previous year.*

Université Laval—Quebéc, Canada, 1959.

Contribution 126. Chemical Compositions of the Grenville and the Southern Part of the Timiskaming-Keewatin Subprovince in Quebec. F. FITZ OSBORNE. Pp. 53–63; figs. 4; tbls. 2. *The ratios of the normative feldspars from the plutonic rocks of Abitibi and the Grenville subprovince are found to be different. However, taking other rocks into account, their average compositions tend to be similar. (Reprinted from Trans. Royal Soc. Canada.)*

Contribution 131. Structural Features of the Northern Part of the Labrador Trough. R. BÉLAND and P. E. AUGER. Pp. 5–15; figs. 4. *The authors show that the Payne Bay-Roberts Lake segment of the Labrador Trough is a semi-isolated basin with the same sedimentary formations cropping out continuously along its rim. (Reprinted from Trans. Royal Soc. Canada.)*

Contributions 132 and 133. Les "Diamants" de Quebec. Collection de Silex Taillés à l'Université Laval. RENÉ BUREAU. Pp. 10. *Two articles concerning the diamond-like quartz crystals of Quebec and the flint implement collection given to Laval University by Dr. Henri-Marc Ami. (Reprinted from Trans. Royal Soc. Canada.)*

Federation of Malaya Geological Survey—Ipoh, 1958–1959.

Economic Bulletin 1.6. Report on Airborne Magnetometer and Scintillation Counter Survey Over Parts of Kedah and Perlis (Area 6). W. B. AGOCS, J. R. PATON, and J. B. ALEXANDER. Pp. 55; pl. 1; composite map 1. Price, $5.00 Malayan. *Generalized report of techniques and results of an airborne magnetometer and scintillation counter survey over parts of Kedah and Perlis. Several moderate anomalies with readings 3.4 times background were noted.*

Economic Bulletin 1.2. Report on Airborne Magnetometer and Scintillation Counter Survey Over Parts of Trengganu and Pahang (Area 2). W. B. AGOCS, J. R. PATON, and J. B. ALEXANDER. Pp. 58; figs. 2. Price, $5.00 Malayan. *Generalized discussion of techniques and results of an airborne magnetometer and radio active survey over Trengganu and Pahang to aid geologic mapping and mineral exploration. Composite map, Area 2, no scale given.*

Missouri Geological Survey—Rolla, 1959.

Bibliography of the Geology of Missouri 1958. J. W. LOENIG. Pp. 36. *Listing of published and unpublished papers and maps concerning the geology of Missouri during 1958.*

Sixth Biennial Report of Division of Geological Survey and Water Resources Covering Period July 1, 1956 to June 30, 1958. T. R. BEVERIDGE. Pp. 38; fig. 1; tbl. 1. *Annual report concerning ground-water, topographic mapping, economic geology, and geologic mapping programs conducted by the State Survey. Of commercial importance were the discoveries of the Pea Ridge iron deposit and Viburnum lead deposit.*

Rept. of Investigations 25. Pennsylvanian (Desmoinesian) of Missouri. W. V. SEARIGHT. Pp. 46; pls. 9; figs. 30; tbl. 1. *A well illustrated description of geology encountered on field trips of Geological Society of America during its Annual Meeting in 1958.*

Montana Bureau of Mines and Geology—Butte, 1959.

Bulletin 10. Directory of Known Mining Enterprises, 1958. KOHLER STOUT, WALTER ACKERMAN, and others. Pp. 80; pl. 1; tbls. 4. *Alphabetical listing of mines by counties.*

Spec. Publication 16. Economics of Secondary Recovery in Montana. D. H. HARNISH, JR. Pp. 4; figs. 3; tbls. 3. *In this reprint from World Oil, November, 1958, it appears that the state's oil reserves could be almost doubled by a successful secondary recovery program.*

Spec. Publication 17 (Geol. Map 2). Geology of the Dryhead-Garvin Basin, Bighorn and Carbon Counties, Montana. J. C. STEWART. Geological map, scale 1 inch : 1 mile, sections, and text on one sheet. *Stratigraphic, structural, and physiographic data is presented on this basin which is bisected by the deeply entrenched Bighorn River.*

New Zealand Geological Survey—Wellington, 1958–1959.

Bull. n.s. 59. Geology of Kaitangata Coalfield. H. J. HARRINGTON. Pp. 131; tbls. 14; figs. 24; maps 13; sections 14. Price, £3. *Well-illustrated report on the stratigraphy, structure, and economic geology of the Kaitangata Coalfield and surrounding regions.*

Bull. n.s. 62. The Geology and Hydrology of Niue Island, South Pacific. J. C. SCHOFIELD. Pp. 28; figs. 12; tbls. Price, 6s. *Geology and hydrology of emerged and terraced limestone reefs which together form Niue Island. A magnetic survey indicates limestone underlain by a caldera-shaped volcanic structure.*

New Zealand Geological Abstracts 1956. B. W. COLLINS. Pp. 395–418. (Reprinted from New Zealand Journal of Geology and Geophysics, Vol. 1, No. 2.)

Uranium Mineralization in the Hawks Crag Breccia of the Lower Buller Gorge Region, South Island, New Zealand. A. C. BECK, J. J. REED, and R. W. WILLETT. Pp. 432–450; figs. 8; tbls. 3. (Reprinted from New Zealand Journal of Geology and Geophysics, Vol. 1, No. 3.) *The main primary mineral is coffinite. Mineralization by solutions has been restricted to the arkosic facies. This area is compared and contrasted with the Colorado Plateau.*

North Dakota Geological Survey—Grand Forks, 1959.

Rept. of Investigation 33. Clays of North Dakota as a Potential Source of Alumina. MILLER HANSEN. Pp. 15; pl. 1. *No deposits meeting commercial requirements for the extraction of alumina from clay were noted from the survey of clay localities in North Dakota.*

Rept. of Investigations 32. Preliminary Report on the Antelope-Madison and Antelope-Sanish Pools. C. B. FOLSOM, JR., C. G. CARLSON, and S. B. ANDERSON. Pp. 38; figs. 20; tbls. 2. *The two pools are in western North Dakota on a small anticlinal fold on the east flank of the Nesson Anticline.*

Production Statistics and Engineering Data: Oil in North Dakota Last Half 1958. Pp. 78. Price, $1.00. *An official publication of production statistics and engineering data for the period indicated.*

Oklahoma Geological Survey—Norman, 1959.

Mineral Rept. 36. The Mineral Industries of Oklahoma in 1957 and 1958. PETER GRANDONE, L. E. EDWARDS, and W. E. HAM. Pp. 24; tbls. 13. Includes a final summary for 1957 and a preliminary summary for 1958.

Oklahoma Geology Notes, Vol. 19, No. 4. Pp. 74–96; 15 articles. Price, 25 cents. *Article by T. W. Amsden on Chilidiopsis Boucot, a recently described brachiopod genus. C. C. Branson discusses some problematical fossils found in Pennsylvanian rocks.*

Ontario Department of Mines—Toronto, 1959.

Bull. 156. List of Maps Outlined on Ontario Department of Mines Index Map No. 1958A. Pp. 13. *A list of maps—not publications; list of all publications in Bulletin 25.*

Geological Circ. 8. Pleistocene Geology of the Hamilton Map-Area. P. F. KARROW. Pp. 6. Geologic map, scale 1:62,500, in pocket. *Preliminary report of Pleistocene deposits of sand and gravel, clay, and peat overlying the Queenston shale and Lockport-Amabel dolomite.*

Pennsylvania Geological Survey—Harrisburg, 1958–1959.

Well-Sample Record 41. Albert No. 1 Well, Adams Township, Snyder County. W. R. WAGNER. Pp. 23. *All but the upper 14 feet of the 5,965 foot dry hole is logged.*

Supplement to List of Publications August 1956. Pp. 3. *Covers geologic and mineral industry reports.*

Geologic Atlas of Pennsylvania 197. Geology of the Precambrian Rocks and Hardyston Formation of the Boyertown Quadrangle. T. V. BUCKWALTER. Pp. 15. Map, scale 1:24,000. *Progress report to May, 1957, including a geologic map of the area and descriptions of the formations.*

Information Circ. 14. The History of Chromite Mining in Pennsylvania and Maryland. NANCY PEARRE and ALLEN HEYL. Pp. 23; figs. 9. *No significant production has occurred since the early 1900's.*

Progress Rept. 155. Oil and Gas Developments in Pennsylvania in 1958. W. S. LYTLE, J. M. BERGSTEN, A. S. CATE, and W. R. WAGNER. Pp. 44; pls. 6; figs. 4; tbls. 8. *During 1958 two wildcats became the state's first deep (Middle Devonian or older) oil and gas producers, respectively.*

Bureau of Economic Geology, The University of Texas—Austin, 1958–1959.

Geologic Quadrangle Map 22. Geology of the Pinto Canyon Area, Presidio County, Texas. D. L. AMSBURY. Price, 75 cents. *A region of Tertiary volcanic and intrusive rocks. Map, scale 1:63,360, accompanying text.*

Rept. of Investigations 38. Internal Structure of the Grand Saline Salt Dome, Van Zandt County, Texas. W. R. MUEHLBERGER. Pp. 23; pls. 6; figs. 2. Price, $1.00. *Extends to the present time Robert Balk's work (1949) on the interior structure of the salt dome.*

Publ. 5905. Symposium on Edwards Limestone in Central Texas. F. E. LOZO, H. F. NELSON, KEITH YOUNG, O. B. SHELBURNE, and J. R. SANDIDGE. Pp. 235; pls. 40; figs. 23. Price, $5.00. *Five papers, one by each author, prepared for use in connection with A.A.P.G. field excursion of March 13–14, 1959.*

Publ. 5910. Bibliography and Index of Texas Geology, 1933–1950. R. M. GIRARD. Pp. 238.

U. S. Geological Survey—Washington, D. C., 1959.

Bull. 1042-S. Geology and Fluorspar Deposits, Big Four Fault System, Crittenden County, Kentucky. G. C. HARDIN, JR., and R. D. TRACE. Pp. 699–724; pls. 2; figs. 2. *Economic deposits of fluorspar are associated with a complex system of steeply dipping normal faults. The ore bodies are the result of fissure filling with some replacement of the early vein material and wallrock.*

Bull. 1045-D. Core Logs from Bristol Cadiz, and Danby Dry Lakes, San Bernardino County, California. A. M. BASSETT, D. H. KUPFER, and F. C. BARSTOW. *Detailed core logs of four holes drilled in the three dry lakes are given.*

Bull. 1046-L. Radioactivity and Uranium Content, Sharon Springs Member of the Pierre Shale Kansas and Colorado. E. R. LANDIS. Pp. 299–319; pls. 4; figs. 2; tbls. 4. Price, 70 cents. *No definite pattern of areal distribution of radioactivity and uranium content is indicated by available data.*

Bull. 1046-P. Uranium Deposits in the Dripping Spring Quartzite Gila County, Arizona. H. C. GRANGER and R. B. RAUP. Pp. 415–486; pls. 4; figs. 19; tbls. 4. *Uranium deposits in the Dripping Spring Quartzite, a formation in the Precambrian Apache group, may have been formed by uranium-bearing hydrothermal solutions emitted by intrusive diabase at a late stage in its differentiation.*

Bull. 1058-C. Geology of Geikie Inlet Area Glacier Bay, Alaska. J. F. SEITZ. Pp. 61–120; pl. 1; figs. 26. *Study of the general geology of the area, including the petrography and petrogenesis of the metamorphic rocks.*

Bull. 1060-B. Geology and Construction-Material Resources of Marion County, Kansas. F. E. BYRNE, C. P. WALTERS, J. L. HILL, and L. RISEMAN. Pp. 63–95; pls. 2; figs. 2; tbl. 1. *Limestone is the local material most useful in construction as aggregate, road metal, riprap, and structural stone. Sand is also used as road metal, and silt might be used as mineral filler.*

SCIENTIFIC NOTES AND NEWS

W. H. BRADLEY has resigned as Chief Geologist of the U. S. Geological Survey and has received a special assignment. He is spending the summer in Europe.

JAMES GILLULY has resigned as Chief of the Fuels Division, U. S. Geological Survey.

W. ROY DUNBAR, mining and geological consultant, Toronto, Canada, recently visited the Allihеis copper mining area in Ireland.

ARMINE F. BANFIELD of Behre Dolbear and Co. has returned from Teheran, having completed a report on the mineral reconnaissance of a 47,000 square mile area in the Kerman region of southern Iran.

LYMAN H. HART, chief geologist of the American Smelting and Refining Co. for the past 13 years, will become consulting engineer for Guggenheim Brothers.

RALPH L. MILLER, formerly chief of Fuels Branch, U. S. Geological Survey, now is technical advisor to the Mexican Geologic Institute for the U.S.G.S. and International Cooperation Administration.

STANLEY H. WARD is now on the staff of the University of California Department of Mineral Technology in Berkeley.

EUGENE CALLAGHAN is in Belo Horizonte, Brazil, working in the St. John d'el Rey mining properties for the M. A. Hanna Company.

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